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THE METALLURGICAL UPGRADING OF AUTOMOTIVE SCRAP STEEL

AMAS LABORATORY

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

In an attempt to solve the problems involved in solid waste disposal, this study investigated developing a procedure for producing high-quality steel from automotive scrap that would be more acceptable to steel makers and foundrymen.

A. W. Breidenbach, Ph.D
Director
National Environmental
Research Center, Cincinnati

A B S T R A C T

Several melting and casting techniques which have been successfully used for purifying refractory metals were evaluated as methods of upgrading automotive scrap steel. These methods include (1) non-consumable electrode arc melting, (2) electron beam melting, (3) vacuum arc melting, (4) vacuum induction melting and (5) electroslag remelting. The removal of copper, chromium and tin from the scrap was of primary interest since these impurity elements are not removed during the steelmaking process but are known to adversely effect the mechanical properties of steel. The optimum conditions for impurity removal by the above melting techniques were determined using simulated auto scrap in small scale melting experiments. Once these conditions were established they were used to melt actual auto scrap obtained from a commercial source. Evaluation of the processed material was made by chemical analysis, metallographic examination and mechanical property measurements.

Electron beam and vacuum induction melting were found to be effective in removing copper and tin from auto scrap but chromium could only be removed when carbon concentrations were low. A procedure was also developed whereby a high grade stainless steel could be prepared during a single vacuum induction heating step. Chromium, tin and aluminum were successfully removed from auto scrap using the electroslag remelting method. A suitable extractant for copper was not found however. A separate study was made in which the effect of various concentrations of copper, chromium, nickel and tin on the mechanical properties of mild steel was determined.

This report was submitted in fulfillment of Grant No. R-801303 by the Ames Laboratory USAEC, Iowa State University under the sponsorship of the Environmental Protection Agency. Work was completed as of June 1973.

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INTRODUCTION

The accumulation of discarded automobiles in junk yards throughout our nation is a much discussed problem today. These auto graveyards are not only unsightly, but they represent a great waste of steel.

The problem of automotive scrap disposal and recyling has been studied extensively by the U.S. Bureau of Mines[1], the Defense Services Administration of the Department of Commerce[2] and by the Environmental Protection Agency[3]. They have found that the accumulated inventory of retired motor vehicles available for recycling is approximately 20 million units. Automobiles account for about 85 percent of this total and represent approximately 21 million tons of steel. It is estimated that 14 million junked cars are already in some stage of the scrap cycle, i.e. auto wrecking, dismantling yards or scrap processors. Eventually these will be recycled and become raw materials for new steel products when the demand exists. The remaining 3 million cars are abandoned and represent a real disposal problem and a waste of a valuable national resource. An additional 6.7 million cars are retired each year of which 5.5 million are processed. This means that the abandoned cars problem is increasing at a rate of 1.2 million per year.

The failure to recycle the steel from car bodies more effectively is largely a metallurgical problem. The presence of copper, tin and chromium, which are important auxiliary metals in every automobile, can not be tolerated in high quality steel since they

adversely affect some of its mechanical properties. Copper and tin are reported to cause hot-shortness in steel during the rolling process.[4] This problem results from an increase in concentration of these elements just under the surface of the steel during the heat treating step (1100°C) necessary prior to the rolling operation. The iron migrates to the ingot surface and is oxidized to iron oxide or scale. The copper and/or tin that remains is in high enough concentrations to be insoluble in the iron and lies in the grain boundaries which parts upon rolling thereby forming cracks. Chromium does not cause hot shortness in steel but along with copper and tin is reported to suppress its ability to be deep drawn.[5] Thus, before it will be economically feasible to reuse larger percentages of automotive scrap in our present steel technology, methods for removing these elements or otherwise neutralizing their adverse effects on the properties of steel must be found.

It was the goal of this study to develop a procedure for producing high quality steel from automotive scrap that would be more acceptable to steel makers and possibly to foundrymen who supply the automotive, building and other large steel-consuming industries. If this goal was achieved, the accumulation of discarded cars in unsightly auto salvage yards across the country would be reduced, and proper use would be made of a major national resource.

CONCEPTUAL APPROACH

Our approach to the solution of this problem has its origin in several melting and casting techniques that have been used in the last two decades for melting refractory metals and alloys used in the various AEC and NASA programs.[6,7] These methods include (1) nonconsumable electrode arc melting, (2) electron beam melting, (3) vacuum arc melting, (4) vacuum induction melting, and (5) electroslag remelting. The first four methods involve the melting of a metal under a reduced pressure and the separation of impurities by vaporization. Electroslag remelting relies on the removal of impurities by extracting them into a molten slag layer that covers the metal during the melting process. Research on the electroslag remelting of auto scrap was funded by a supplementary grant from the Rockefeller Foundation for the 1971-1972 period. The results obtained are included in this report because of its relevance to our overall approach to the solution of the problem.

Our investigation consisted of a two-step approach. The optimum conditions for the impurity removal by the above listed melting techniques were first determined using simulated auto scrap in small scale melting experiments. The conditions of pressure over the melt, the temperature of the molten pool and the retention time necessary for removing copper, tin and chromium for each method were determined. Evaluation of the processed material was made by chemical analysis, metallographic structure and mechanical properties. It was hoped that the second step of the investigation would consist of the development of a practical process for refining actual auto-

motive scrap steel in several hundred pound quantities. This part of the objective was not accomplished due to the extended time that was needed to develop the optimum conditions for impurity removal. One thousand pounds of ground-up pieces of automobile scrap were obtained from a commercial source and a portion of it melted into ingot form using the conditions developed for the simulated material.

Melting of steels under low pressures has been shown to be advantageous and quite acceptable to the metallurgical industry especially in the specialty steel field.[8-11] Our experience has shown that impurities which have vapor pressures roughly 100 times greater than that of the solvent metal can be removed almost completely by either arc melting or electron beam melting under vacuum. Those impurities having vapor pressures greater by only a factor of 10 can in many instances also be removed, but experimentation is necessary in order to determine their behavior. Figure 1 shows the vapor pressures of the common impurities in auto scrap steel together with that of iron. These data are the most recent available in the literature and were compiled by the Lawrence Radiation Laboratory, Berkeley, California.[12] As can be seen from Figure 1, the vapor pressures of copper and tin are more than 10 times that of iron at its melting point. In our original proposal we stated that chromium could undoubtedly be removed from iron because its vapor pressure was 41 times greater than iron. We obtained this value for the vapor pressure of chromium from the International Critical Tables which we now know to be in error.

The theoretical use of vacuum melting for the removal of copper, tin and possibly chromium from iron and steel may be illustrated as

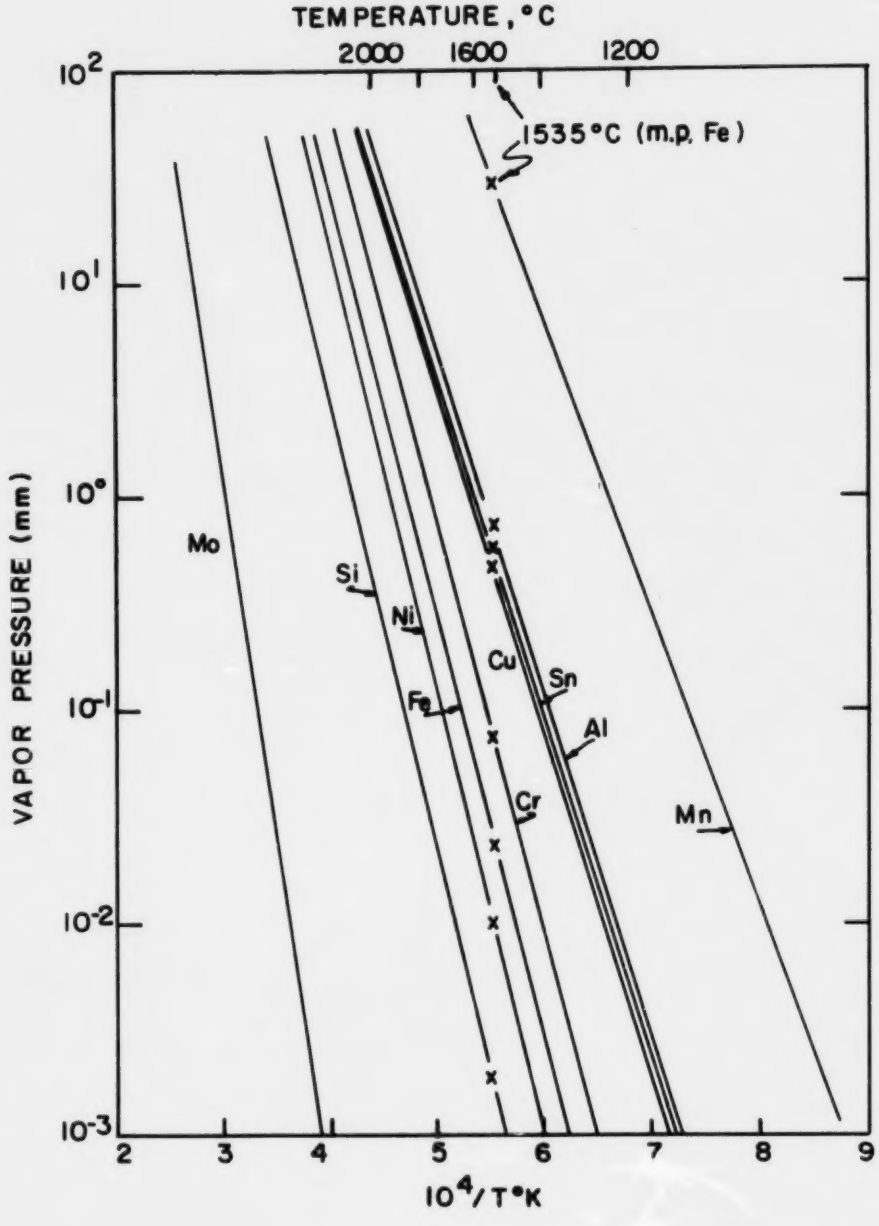


Fig. 1 Vapor pressure of iron and the common metal impurities found in auto scrap.

follows: The vapor pressure of iron at its melting point (1535°C) is 2.6×10^{-2} torr while the vapor pressure of copper at the same temperature is 4.3×10^{-1} torr which is a factor of 17 greater. The activity coefficient of copper (γ_{Cu}) at infinite dilution in iron is 8.0 at the melting temperature of iron.[13,14] Consequently,

$$\frac{P_{Cu}}{P^{\circ}_{Cu}} = \gamma_{Cu} N_{Cu} \text{ and } P_{Cu} = 8.0 N_{Cu} P^{\circ}_{Cu}$$

where P_{Cu} and P°_{Cu} are the vapor pressures of copper in the melt and in the pure state respectively, N_{Cu} is the atom fraction of copper, and γ_{Cu} is the activity coefficient. Thus for $N_{Cu} = 0.01$ to 0.001 (corresponding approximately to 1.0 to 0.1 w/o copper in iron), we find $P_{Cu}/P^{\circ}_{Cu} = 0.08$ to .008. Since $P^{\circ}_{Cu} = 4.3 \times 10^{-1}$ torr, $P_{Cu} = 3.4 \times 10^{-2}$ torr to 3.4×10^{-3} torr. Then since $P^{\circ}_{Fe} = 2.6 \times 10^{-2}$ torr, we find $P_{Cu}/P^{\circ}_{Fe} = 1.3$ to 0.13. These values indicate that under equilibrium conditions 1.3 to 0.13 atoms of copper will be volatilized for each iron atom that is volatilized. This should lead to the effective removal of copper with only a minor loss of iron. The vapor pressure of tin at the melting point of iron is 4.6×10^{-1} torr which is a factor of 18 greater than the vapor pressure of iron at this temperature. From the most recent data available, chromium has a vapor pressure of 6.8×10^{-2} torr at the melting point of iron which is only a factor of 2.6 greater than that of iron. From this new data it is therefore reasonable to assume that copper and tin will be removed with only a minimal iron loss but the removal of chromium may be more difficult than originally expected since its true vapor pressure is more nearly that of pure iron.

The elimination of residual elements from iron melts by means of vacuum induction heating has been studied by several investi-

gators.[15,16,17] Olette has shown that when minor components are distilled from iron melts, iron obeys Raoult's law and γ_{Fe} is very close to unity. The solute Y at low concentrations obeys Henry's law and γ_Y is nearly constant and equal to γ_Y°; the activity coefficient of Y when it is present in low concentrations. It would be equal to 1 if the solution were ideal. Under such conditions the evaporation coefficient, α, is equal to,

$$\gamma_Y^\circ \, (P_Y^\circ / P_{Fe}^\circ) \sqrt{55.85/M_Y}$$

where M_Y is the atomic weight of element Y. The values Olette obtained for α for metals in low concentrations in iron at 1600°C are shown in Table I. The larger the value of α for a given impurity atom the more easily it will be removed from iron solutions when heated in vacuum. The value of α for iron is taken as 1.

Table I.

Element	Evaporation Coefficient, α
Cu	125
Sn	9.1
Cr	3.3
Al	1.4
Mn	900
Si	0.07
Ni	0.7
Co	0.5

These data show that copper, tin, manganese and possibly chromium could be removed from iron by heating in vacuum.

Copper and tin are valuable metals and their recovery would effect the cost of a commercially feasible recycling process. Copper and tin should be removed as metal vapor and collected as a condensate on the walls of the melting furnace. Although no efforts were made to remove the copper and tin from the condensates during this work, no particular difficulty should be encountered in retrieving them by dissolution in mineral acid and then recovering the copper and tin by electrolytic processing.

EXPERIMENTAL PROCEDURE AND RESULTS

During the first year of this project many melts of simulated auto scrap were made using the melting methods mentioned above. Each melt was chemically analyzed for those impurities that are considered detrimental to the mechanical properties of steel. From these data the conditions for melting were varied and the effect of time in the molten state, pressure over the melt and temperature were studied for those melting procedures employing a reduced pressure. The ingots prepared by electroslag remelting were also analyzed and efforts made to correlate the composition of the extractant slag with impurity removal.

In June of 1972 a quantity of actual auto scrap was obtained from a commercial source and it was melted using the most favorable conditions developed for the simulated material. In general, the removal of impurities from the actual scrap paralleled those achieved from the simulated scrap with a few exceptions which will be discussed later.

There is some uncertainty of the effects of copper, tin, chromium and nickel on the mechanical properties of steel as reported in the literature. Therefore, as an important part of our research effort, a complimentary study was made of the effects of those elements on the drawing and tensile properties of 1005 steel.

1. Compacting of Scrap for Use as Melt Stock Material

One of the problems that became apparent immediately upon initiation of our investigation was how to sample an automobile hulk so that it is representative. This is quite important in order to perform the experimental work on a small scale and later translate

the results to a large pilot plant or industrial operation. In an attempt to obtain a uniform material for our research and melting experiments we obtained an average chemical analysis of shredded auto scrap (Lurmet) from Dr. Richard Burlingame, who is director of research and development at Ogden Metals, Cleveland, Ohio. The average analysis of six 10-ton melts of the scrap is shown in Table II along with the concentration of these impurities desired by metal fabricators.

Table II. Concentration of Impurities in Shredded Auto Scrap and Level Desired by Fabricators[5]

Elements	Concentration, w/o	
	Average of six 10-ton melts of Auto Scrap	Desired Level of Impurity*
Chromium	0.15	0.03
Copper	0.25	0.06
Molybdenum	0.015	0.01
Nickel	0.11	0.03
Tin	0.035	0.01

* These values can be combined. For example, the copper and tin content could total 0.07 w/o with copper being present in a lower concentration than 0.06 w/o and the tin content greater than the 0.01 w/o shown in the Table).

Using this analysis we prepared several small 45g alloy buttons for use in studying impurity removal by nonconsumable electrode arc melting.

(A) Preparation of Simulated Auto Scrap Compacts. Approximately 425 compacts measuring 2.8 cm x 1.9 cm x 30.5 cm and weighing 1 kg each, were prepared and used as melt stocks and consumable

electrodes in the vacuum melting and electroslag melting experiments. Mild steel sheet containing approximately 0.05 w/o carbon (1005 steel) and low levels of other impurities was cut into strips and shredded in a high speed mill. This steel is quite similar to that used in the bodies of automobiles and after shredding is similar to the form obtained from the auto shredders located in Cleveland and Detroit. Wires of the various impurity elements were prepared in 30.5 cm long sections and having diameters dictated by the desired composition. These were pressed together with the shredded pieces of mild steel thereby forming a compact of simulated auto scrap. Several of these compacts (1 kg) and alloy buttons (45 g) were melted under 76 cm of argon gas pressure (no impurity removal) and chemically analyzed. The results showed the compacts to contain the same concentration of impurities as the average of the tonnage melts shown in Table II. In addition to the elements shown in Table II these compacts contained approximately 0.015 w/o aluminum, 0.3 w/o manganese, 0.008 w/o nitrogen, 0.03 w/o oxygen and 0.03 w/o silicon which were present as impurities in the mild steel.

(B) Preparation of Actual Auto Scrap Compacts. In order to determine how actual auto scrap would perform as melt stock in the various melting procedures, approximately 450 kg were purchased from the Eidal International Corp. of Albuquerque, New Mexico. This scrap had been especially processed in a vertical shaft hammer mill to a particle size less than 3.8 cm. Some of the pieces were too large for our compacting equipment so these were hand sorted and further processed in our chopping and cutting equipment. The entire

batch was then homogenized as much as possible by mixing in a Y type blender.

Test runs were made using this material and the finished 1 kg compacts exhibited a structural quality superior to those produced from the simulated scrap. Several of these compacts were melted under one atmosphere of argon gas and a center section cut from each resulting ingot for chemical analysis. Average of these analyses are listed in Table III.

Table III. Analysis of Eidal Auto Scrap

Concentration, w/o Elements									
C	O	Al	Cr	Cu	Mn	Mo	Ni	Si	Sn
0.35	0.05	0.004	0.026	0.088	0.38	0.013	0.11	0.15	<0.005

These results show that the Eidal scrap was appreciably lower in copper, chromium, molybdenum and tin than the average analysis of 10 ton melts in Table II. The impurity wires described above were therefore employed with the real scrap when preparing compacts. This addition of impurities did not change the melting characteristics associated with the consolidation of actual scrap material. Approximately 35 compacts of this material weighing 1 kg each were produced for the various melting experiments.

2. Methods of Reduced Pressure Melting

The methods used for reduced pressure melting of simulated auto scrap were (A) nonconsumable electrode arc melting, (B) electron beam melting (C) vacuum arc melting, and (D) vacuum induc-

tion melting. The ingots obtained from each experiment were sampled and chemically analyzed for copper, tin, chromium, aluminum, manganese, molybdenum, nickel, silicon, carbon, oxygen and nitrogen. In this manner the effect of a small change in the melting condition could be determined and either incorporated or rejected as a parameter for melting. In most cases, the overall yield of iron in the final ingot was also determined.

(A) Nonconsumable Electrode Arc Melting. The furnace used for the nonconsumable electrode arc melting of simulated auto scrap is shown in Figure 2. A series of six buttons of simulated auto scrap weighing 45 g each was nonconsumably arc melted under different partial pressures of argon gas. Melts were made at 25, 12.5, 5, 2.5, 1.2 and 0.6 cm (of Hg above absolute) and the common impurities traced by chemical analysis. A small amount of manganese was volatilized by this technique but the copper, tin and chromium contents were essentially unchanged. Additional efforts were made to melt simulated buttons of auto scrap at lower pressures than 0.6 cm of argon but a stable arc condition could not be established. In this type of melting the electrode is water-cooled and the only means of stabilizing the dc arc is by vapors coming off of the melt or the electrode. Essentially no vapor is generated from the electrode since it is water cooled and as a result melts cannot be made at the low pressures necessary for impurity removal. Although nonconsumable arc melting did not appear to be promising as a refining method it did assure us of a suitable method of making up homogeneous alloys of nominal composition without any loss of the desired alloy agent.

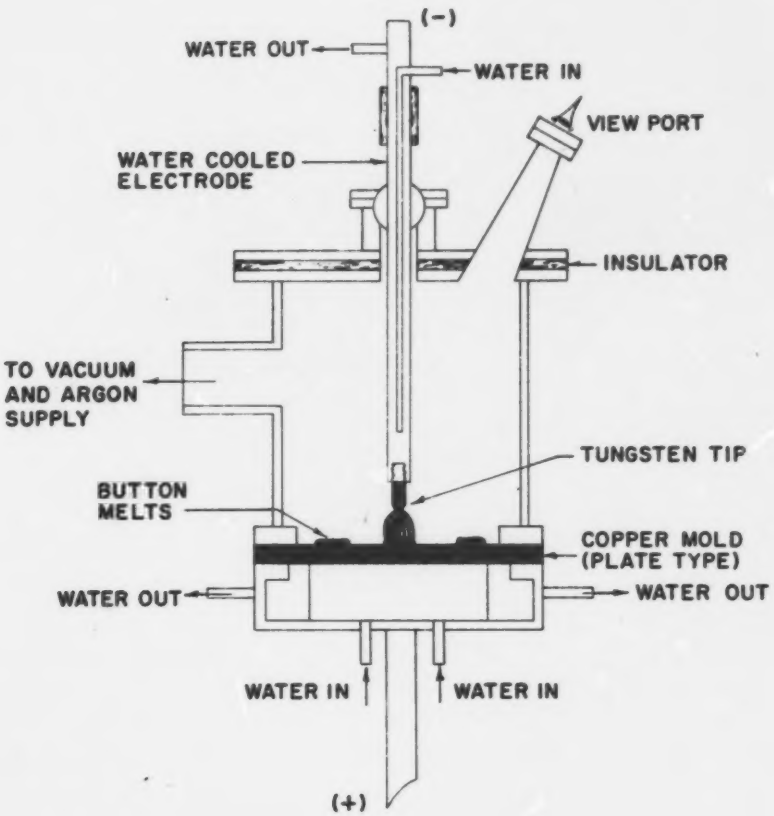
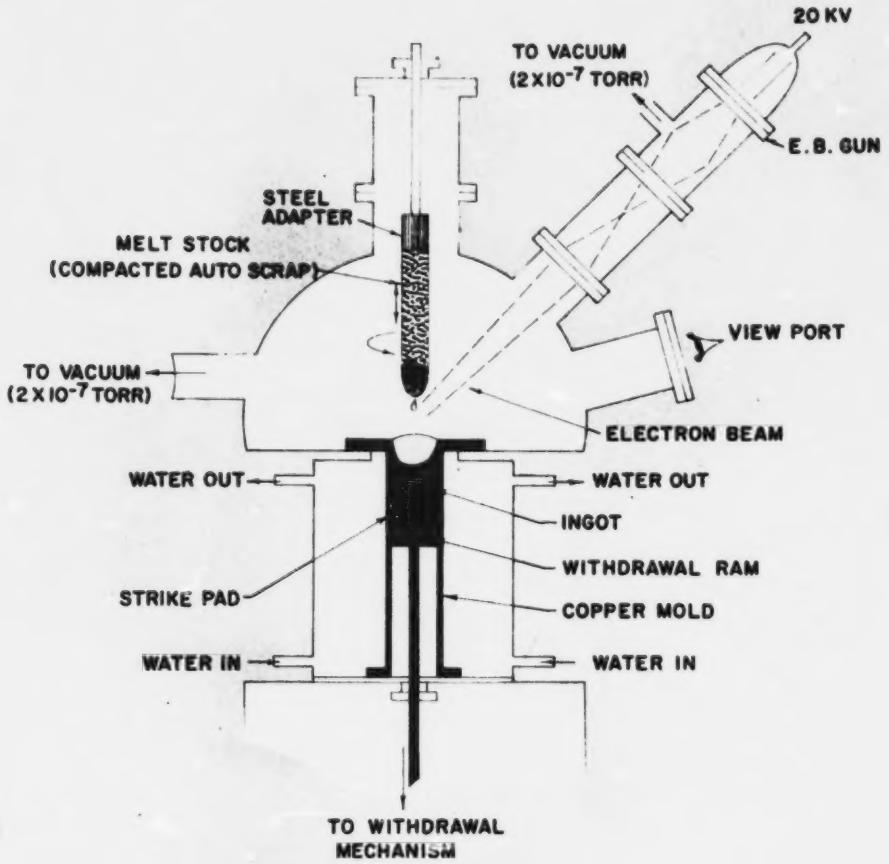


Fig. 2 Nonconsumable electrode arc furnace used for small scale alloy preparation.

(B) Electron Beam Melting. Our first experiments of electron beam melting simulated auto scrap were made on four alloy buttons weighing 45 g each. These melts were made in a small 9 kW furnace under a pressure of 2×10^{-6} torr. The time at which these alloys were held molten (retention time) was varied and the change in chemical composition, before and after melting, determined. The data obtained were quite encouraging since 90% of the copper and tin was removed along with some carbon, oxygen and manganese. The chromium and nickel compositions were essentially unchanged (less than 2% decrease) which was consistent with the revised vapor pressure data obtained from Lawrence Radiation Laboratory. These melts were made very slowly and the temperature was not raised much above the melting point of iron (1535°C). Approximately 8% of the iron was lost from the melt and condensed on the furnace wall where it could be collected.

(a) Simulated Auto Scrap. During the first year, twenty-one experimental melts of simulated auto scrap compacts weighing 1 kg each were made. These melts were made in our 60 kW electron furnace of the remote gun design as shown schematically in Figure 3. This unit was equipped with a 5.0 cm diameter water-cooled copper mold. A series of four melts were made at each of three temperatures using melt rates of approximately 1, 2 and 4 kg per hour. The temperatures used were 1600, 1700 and 1750°C. The data obtained from these melts are shown graphically in Figures 4, 5, and 6. The copper content can be reduced to less than the 0.06 w/o desired using a melt rate of 1.4 kg per hr at 1600°C (10 kW), 1.8 kg per hr at 1700°C (12 kW) and



ELECTRON BEAM MELTING
OF AUTO SCRAP

Fig. 3 Electron beam melting furnace used to melt auto scrap.

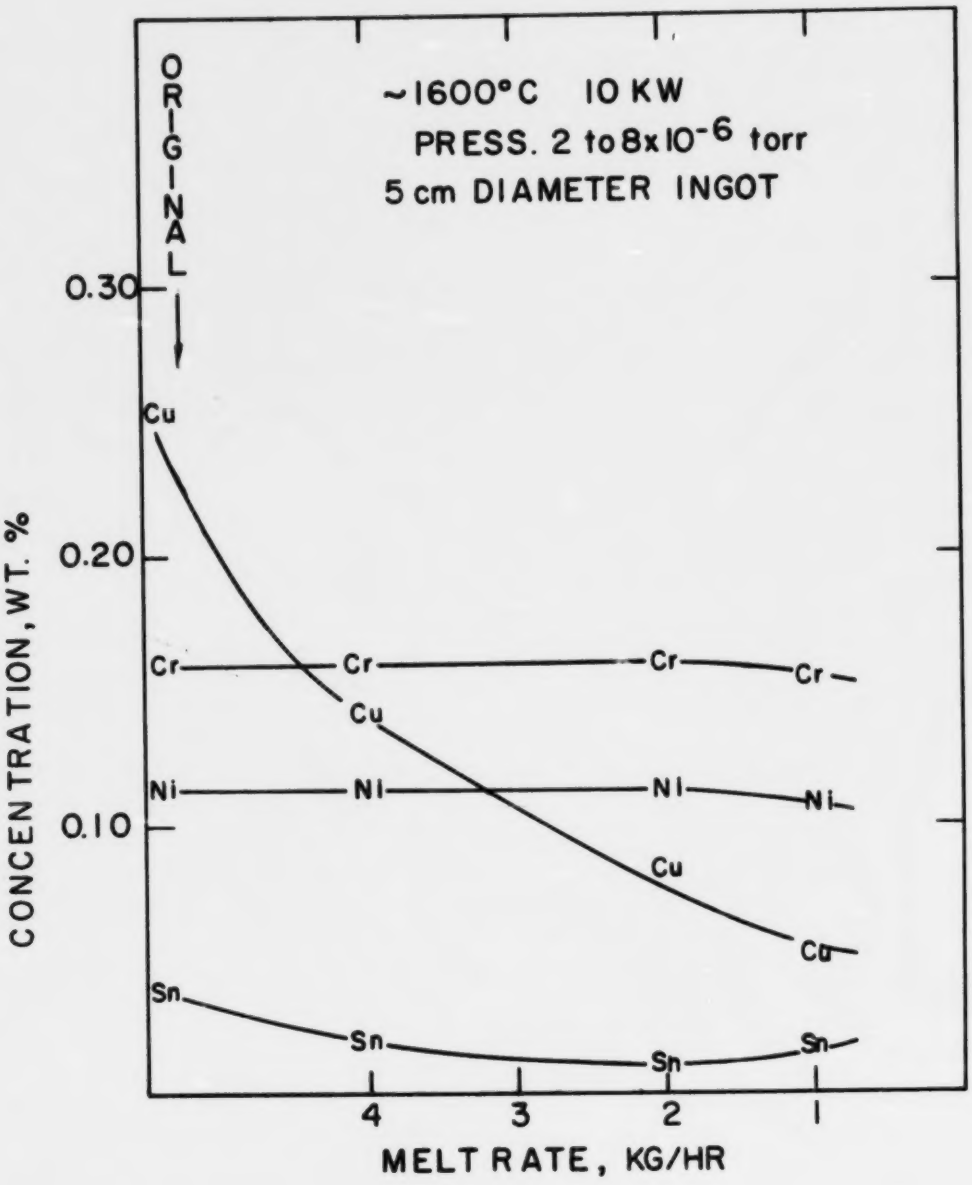


Fig. 4 Impurity concentration vs melt rate for electron beam melting of simulated auto scrap at ~1600°C.

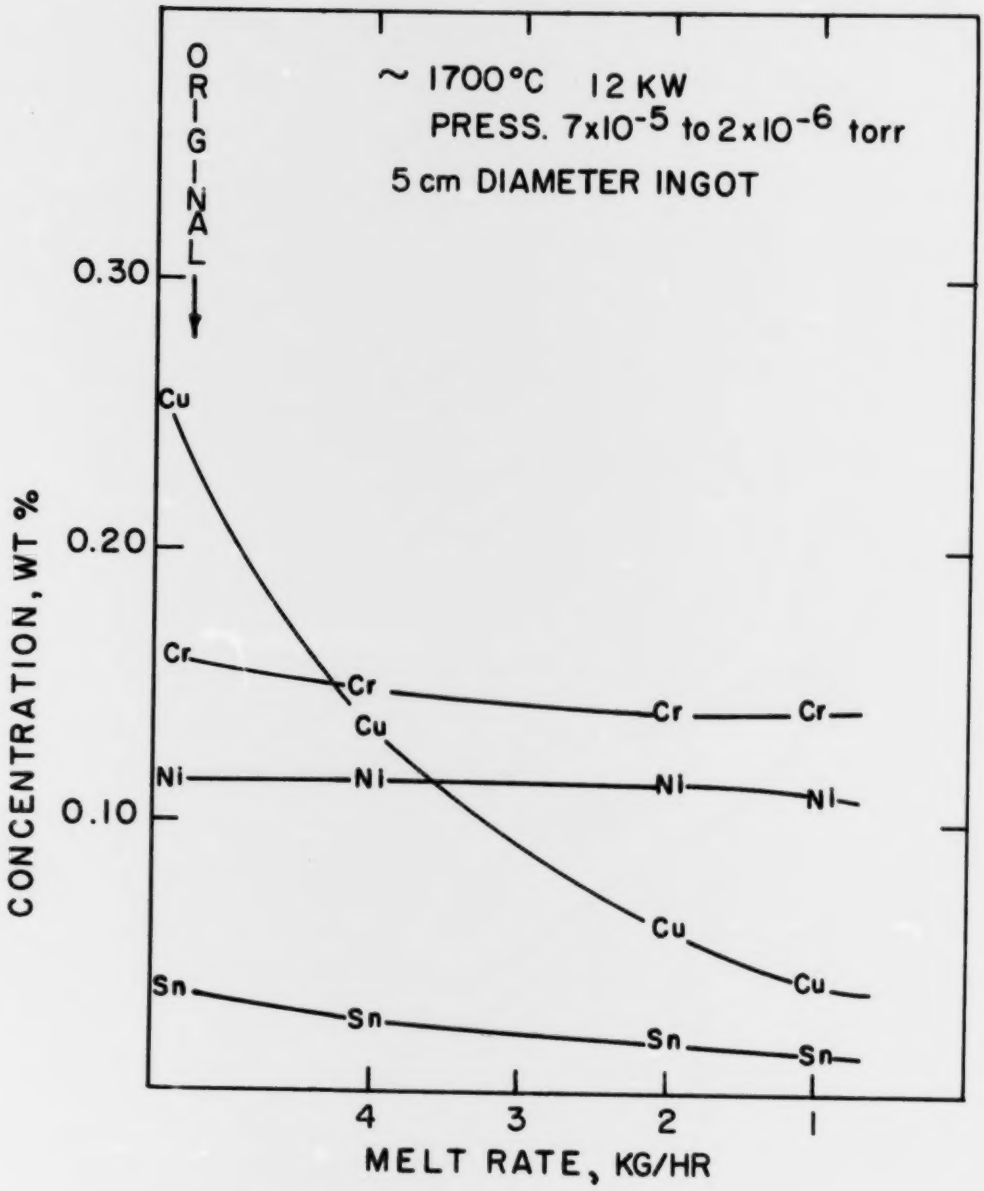


Fig. 5 Impurity concentration vs melt rate for electron beam melting of simulated auto scrap at ~1700°C.

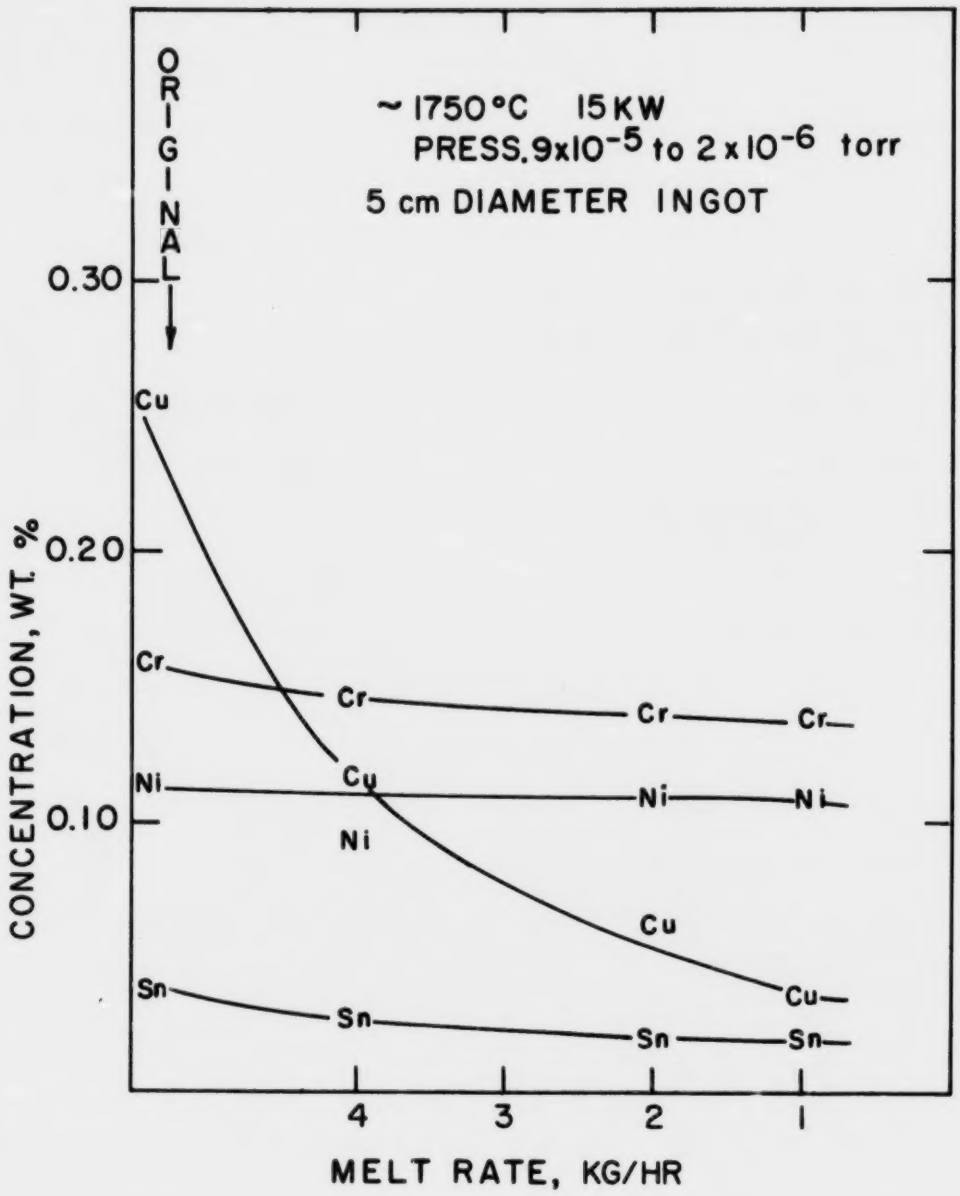


Fig. 6 Impurity concentration vs melt rate for electron beam melting of simulated auto scrap at ~1750°C.

2.3 kg per hr at 1750°C (14 kW) in our furnace. The original concentration of tin in the simulated compacts is 0.035 w/o. At the same melt rates needed to decrease the copper to 0.06 w/o, the concentration of tin decreased to 0.01 - 0.02 w/o. This concentration of tin in steel is also acceptable for fabrication.

In a special experiment, a compact of steel containing 0.25 w/o copper and 0.25 w/o tin was prepared. It was electron beam melted at ~1700°C (12 kW) at a rate of 1.8 kg per hour. The copper content of this ingot was 0.05 w/o while the tin content was 0.03 w/o. This represents a 88% reduction in the tin concentration compared to a 50% reduction when the original concentration was only 0.035 w/o. This difference in the percentage removal illustrates the expected increase in activity of the impurity atom when it is present in higher concentrations in the solvent metal.

The chromium, silicon and nickel contents of the simulated compacts melted at the three temperatures were decreased only slightly (less than 5%) by electron beam melting. The manganese content was decreased from 0.3 w/o to less than 0.1 w/o at a melt rate of 4 kg per hr at 1600°C and to less than 0.02 w/o at a melt rate of 1 kg per hr at 1750°C.

The carbon, nitrogen and oxygen contents of the simulated auto scrap was decreased in each electron beam melting experiment. The carbon content was decreased from 0.050 to 0.025 w/o, the nitrogen from 0.008 to less than 0.0025 w/o and the oxygen from 0.03 to less than 0.005 w/o. A Quad 150 Residual Gas Analyzer manufactured by Electronic Associates Inc., Palo Alto, California was also used in

some experiments to monitor the gases coming off the melt during the melting step. Substantial increases in peaks having atomic mass units of 14, 18, 28 and 44 were noted during melting and particularly when the melt stock was withdrawn from the beam and the maximum pool temperature was achieved. This indicated large amounts of nitrogen, carbon monoxide and carbon dioxide evolving from the melt which is consistent with the observed decreases of carbon, oxygen and nitrogen. Efforts to observe metal ions leaving the melt using the gas analyzer were only partially successful. Manganese metal at mass 55 could readily be detected and distinguished from iron having a mass of 56 with isotopes at 54, 57 and 58 amu. Copper peaks could be seen only in special experimental melts in which the copper content of the compacts was 4 w/o. The electronic ionizer, which is the sensing assembly for the gas analyzer, was located about 76 cm from the molten pool because of a heat problem. This distance is sufficient for the copper to condense on the furnace wall prior to reaching the ionizer. Efforts to observe tin coming from a melt containing the standard 0.035 w/o Sn concentration were unsuccessful.

In an effort to remove chromium and nickel from the simulated auto scrap, various inorganic salts were added during electron beam melting in an attempt to form compounds of these elements that have higher vapor pressures than the metals themselves. In separate experiments 5 to 10 grams of CaF_2, MgF_2, NaF, $CaCl_2$ and NaCl were placed in a 0.64 cm diam. tube and sealed at both ends. This tube was crimped every 2.5 cm along its length and then pressed together with the simulated scrap into a compact. As the compact was melted

by the electron beam a small amount of the molten salt was continually added to the molten steel. The chemical analysis of these melts showed that in all cases the copper and tin concentrations was lowered as usual to 0.06 and <0.01 w/o respectively, but no change was observed in the chromium or nickel contents within the experimental limits of the chemical analysis.

In December of 1972, Dr. G. K. Bhat of Carnegie-Mellon University visited our Laboratory as a consultant for this project. His primary purpose was to help us with the electroslag remelting approach to the purification of scrap steel. However, in our discussions he suggested that the removal of chromium from the steel scrap may be enhanced by vacuum melting in the presence of an excess of oxygen. This approach was pursued by adding 5 grams of Fe_2O_3 to a 0.64 cm diameter steel tube and compacting it along with 1 kg of simulated scrap as was done with the inorganic salts described above. This compact was electron beam melted at approximately 1650°C under a pressure of 2×10^{-5} to 2×10^{-6} torr. Upon chemical analysis of the resulting ingot the copper and tin concentrations were decreased to their usual levels of 0.06 and <0.01 w/o while the chromium content was lowered from 0.16 w/o to 0.009 w/o and the nickel from 0.12 w/o to 0.042 w/o. The carbon content of this ingot was only 0.001 w/o and the oxygen content was 0.10 w/o. This experiment was repeated several times with similar results except the decrease in the nickel content was not consistent. In some experiments a substantial decrease was noted while in others decreases of only 10% were observed. From the data reported by Winkler and Bakish[18] it is believed that chromium in the presence of carbon forms a nonvolatile chromium carbide and stays in the

melt. Upon the addition of excess oxygen in the form of Fe_2O_3 (the major component of rust) the carbon is removed as carbon monoxide and the chromium is vaporized as metallic chromium. When nickel was removed from the melt it was probably due to the formation of a volatile nickel oxide in the presence of excess oxygen.

A series of experiments were made in which different amounts of oxygen were added as Fe_2O_3 to the compacts of simulated scrap in an effort to determine the minimum oxygen needed to achieve chromium removal. The results of these experiments are shown in Table IV.

Table IV. Effect of Oxygen Addition on Chromium Removal During Electron Beam Melting of Simulated Auto Scrap

Grams of Oxygen Added as Fe_2O_3 to 1 kg Compact of Simulated Auto Scrap	Analysis of E.B. Melted Ingot, w/o		
	C	O	Cr
none	0.050	0.030	0.160
0.21	0.001	0.018	0.120
0.48	0.001	0.057	0.063
1.35	0.002	0.085	0.012
1.50	0.001	0.104	0.009

The amount of iron as well as impurities lost by vaporization during the electron beam melting of simulated scrap varied depending on the temperature of superheat, retention time and pressure over the melt. At 1600° and 1700°C weight losses varied from 5 to 8% except for one melt at 1700°C that was held at temperature for 1.1 hrs. The loss of metal from the pool in this case was 10.5%. At 1750°C the losses were higher, varying from 7% for a melt rate of

4 kg per hr to 19.7% for a melt rate of only 1 kg per hr.

The evaporation losses of iron during vacuum melting can be predicted from the Langmuir equation,[19]

$$G = 48 \times 10^{-3} P\sqrt{\frac{M}{T}}$$

where G is the rate of evaporation of metal in g/cm^2 - sec, P is the vapor pressure (in torr) of iron at temperature T° Kelvin, and M is the atomic weight of iron. This evaporation rate is for furnace pressures of less than 0.01 torr. Using this equation the evaporation losses at different temperatures of a 5 cm diameter iron ingot being melted at a rate of 2.2 kg per hr are shown in Table V. The values obtained agree well with those actually observed at 1700 and 1750°C. At 1600°C the iron losses encountered were markedly higher than those indicated by the calculation.

Table V. Calculated and Actual Losses of Iron at Various Temperatures During Electron Beam Melting

Temperature, °C	Percent Weight Loss	
	Calculated	Actual
1600	1.9	5
1650	3.8	-
1700	6.9	6
1750	11.8	10
1800	19.6	-

It should be noted that the metals evaporated from the molten pool were collected on the furnace wall or condenser plates located around the molten pool. The power consumed when iron is evaporated

necessitates keeping this volatilization to a minimum in order to maximize the efficiency of the melting operation.

(b) Actual Auto Scrap. Shortly after the 450 kg quantity of actual auto scrap was received from the Eidal Corporation and blended in our Laboratory, three 1 kg compacts were prepared from randomly chosen portions. Upon electron beam melting excessive degassing occurred which caused splattering in the melt area resulting in metal yields of only 65 to 75%. By use of the residual gas analyzer the gases given off were identified as carbon monoxide and/or nitrogen (a.m.u. 28) and carbon dioxide (a.m.u. 44). From the analysis of the starting material (Table III) one would expect large quantities of carbon monoxide to be liberated during melting because of the 0.35 w/o carbon present and the oxygen present on the metal surface as Fe_2O_3. Analysis of the ingot prepared from these first efforts is shown in Table VI. As previously mentioned,

Table VI. Chemical Analysis of Electron Beam Melted Actual Auto Scrap.

Element	Concentration, wt %
C	0.002
O	0.020
N	0.007
Al	0.001
Cr	0.020
Cu	0.005
Mn	0.005
Mo	0.006
Ni	0.020
Si	0.014
Sn	<0.005

the copper, tin, chromium, nickel and molybdenum content of the material received from the Eidal Corporation is not representative of large quantities (Table II). As a result, melt stocks containing actual auto scrap and the appropriate additions of these elements were used in all subsequent melts of actual auto scrap.

In an effort to decrease the degassing and resulting splatter which decreases the metal yield during electron beam melting, a series of experiments was made in which aluminum was added in various forms to chemically unite with the excess carbon monoxide thereby decreasing the amount of gas evolved and "killing" the melt. Aluminum was added as powder or wires pressed into the compacts or as paint sprayed onto the surface of the compact which was then heated to 400°C. Best results were obtained when a fine aluminum wire weighing 0.7 g was added to each 1 kg compact. In these experiments the steel recovery was 88 to 90% and the copper and tin contents were decreased to 0.07 and 0.015 w/o respectively. The chromium content was not decreased as expected since excess oxygen was not present. The carbon contents of these melts varied from 0.05 to 0.10 w/o.

In an effort to remove the chromium from actual auto scrap and still retain good metal yields, two melts of 1 kg each were made in which aluminum wire was added to the actual scrap containing impurity additions, along with excess oxygen in the form of Fe_2O_3. These experiments resulted in 5 cm diameter ingots that contained 0.0065 w/o carbon, 0.08 w/o chromium, 0.08 w/o copper, less than 0.01 w/o tin and 0.1 w/o nickel. The metal yield of these melts was 80%. In this series, a third melt was also made in which four compacts were clustered and melted into a 7.6 cm diameter ingot.

The analysis of this larger ingot was quite similar to that obtained on the 5 cm diameter ingots and a metal yield of 79% was realized.

In Figure 7, the decrease in chromium content achieved by electron beam melting is plotted against carbon content. These data were taken from melts in which both simulated and actual scrap were used. The carbon and consequently the chromium content was varied by adding different amounts of Fe_2O_3 to the compacts prior to melting.

(C) Vacuum Arc Melting (C. V. Owen). The vacuum arc furnace used in these experiments is shown schematically in Figure 8. It is a 50 kW unit in which ingots up to 7.6 cm in diameter can be prepared. The furnace pressure can be varied from atmospheric pressure to 2×10^{-6} torr. All melts were made at the top of the water-cooled mold employing continuous bottom withdrawal of the ingot thus providing the optimum conditions for the impurity vapors to escape from the melt area.

The effect of pressure and rate of melting on the removal of the various impurities present in the simulated auto scrap was studied. The melting rate was varied from 0.17 to 0.54 kg/min and the pressure in the furnace during the melting from 8×10^{-2} torr to 5×10^{-4} torr. Each ingot was chemically analyzed for copper, tin, chromium, nickel and molybdenum content. The results of melting at 5×10^{-3} to 5×10^{-4} torr are shown in Figure 9 where the impurity content is plotted against the melting rate. The molybdenum content of these ingots remained unchanged from the 0.015 w/o present in the simulated compacts used as electrodes. The data shown are for the lowest pressure used during vacuum arc melting but similar results were achieved at higher pressures.

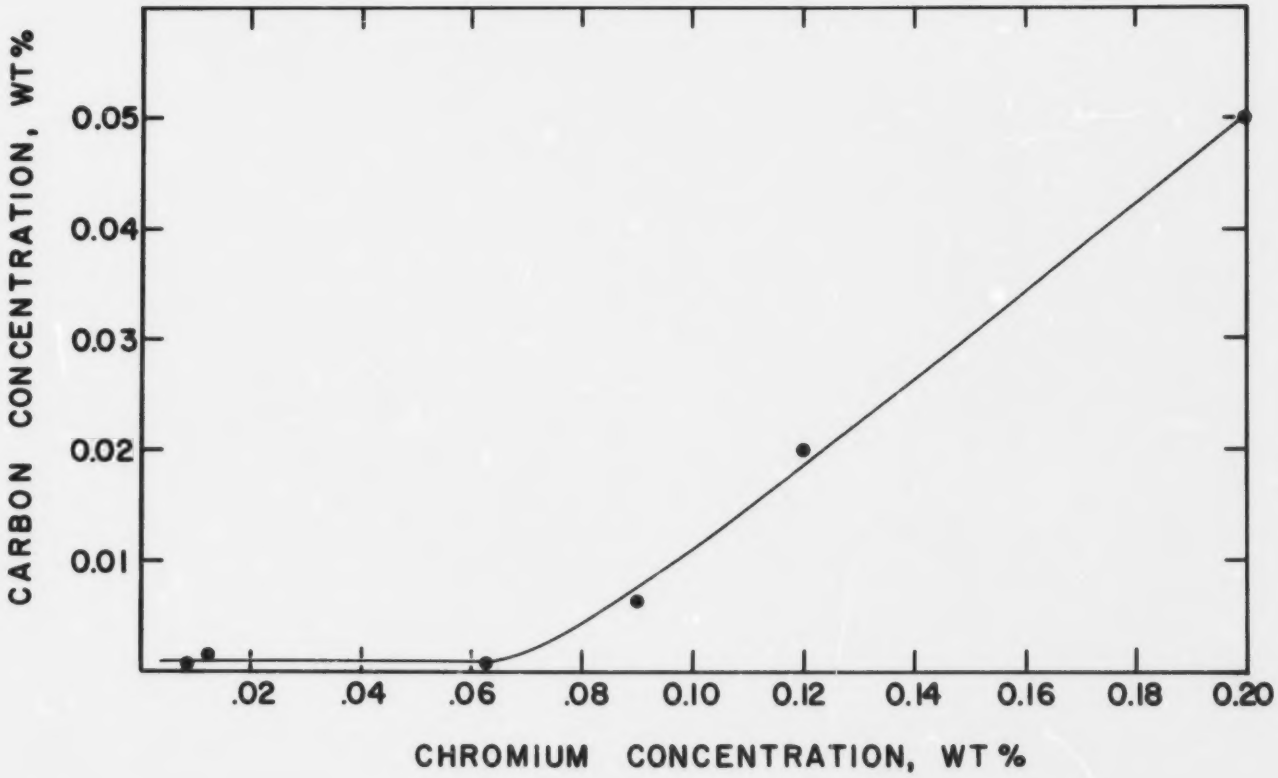
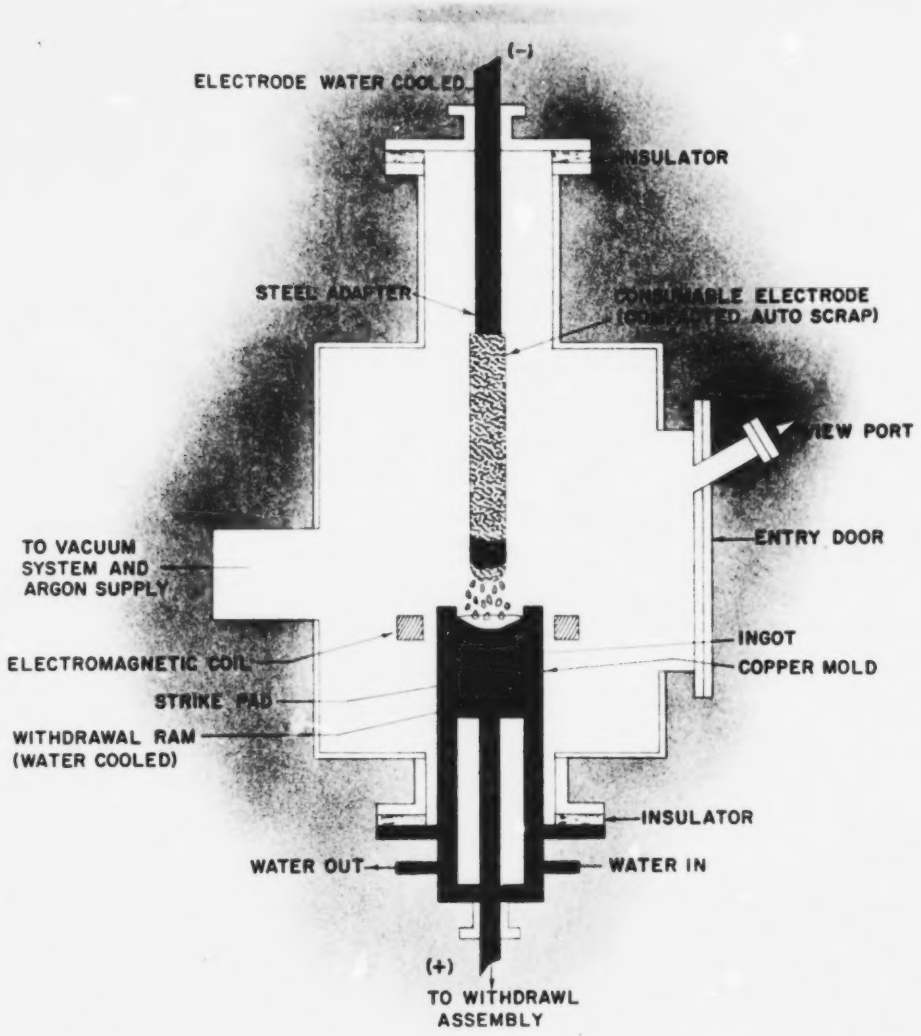


Fig. 7 Plot of carbon content vs chromium content of simulated and actual auto scrap after electron beam melting.



CONSUMABLE VACUUM ARC MELTING
OF AUTO SCRAP

Fig. 8 Vacuum arc melting furnace used to melt auto scrap.

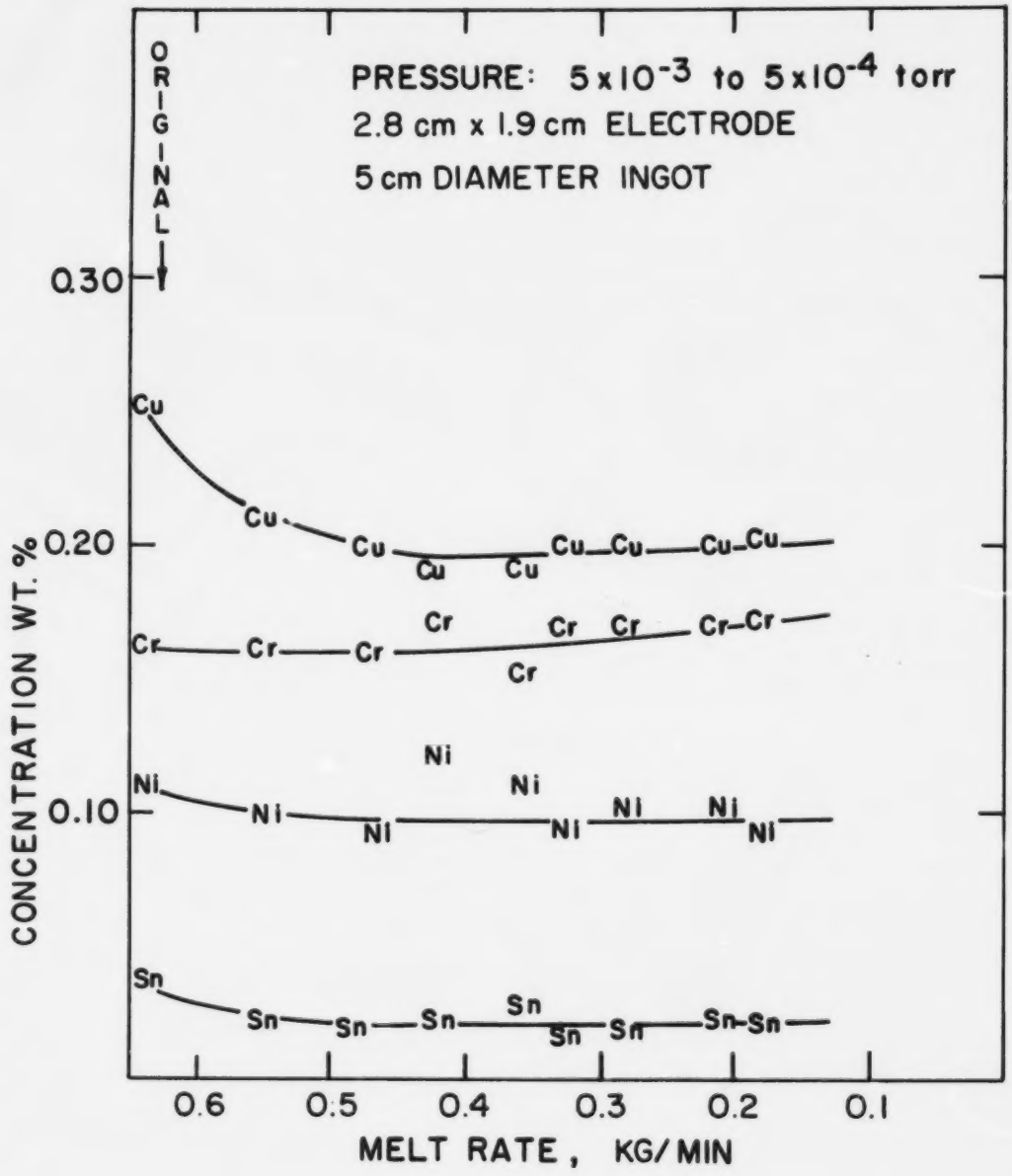


Fig. 9 Impurity concentration vs melt rate for vacuum arc melting of simulated auto scrap.

From the data in Figure 9 it can be seen that little if any impurity removal has been accomplished at the pressures and rates of melting employed.

Butler and Morgan[20] ascertained that certain parameters had to be accurately determined before purification and consolidation of tungsten, tantalum and niobium could be achieved by high vacuum arc melting. They list arc length, electrode composition (primarily diameter and density) system pressure and arc current as variables having the biggest influence on arc behavior with the latter having the greatest effect. They further stated that when all parameters are controlled within certain limits, purification equivalent to that obtained by electron beam melting can be accomplished using the consumable electrode vacuum arc technique.

Experimental melts were made in which the parameters mentioned above were varied in an attempt to determine ideal system and arc conditions in order to achieve a very slow pulsating type melt. It was believed the only way the impurities of interest could be removed was by employing longer retention times in the molten state. These efforts met with only limited success and melting rates were decreased by only one-third of those previously achieved. Ingot quality decreased significantly as the melt-off rate was reduced and analysis of the ingots showed little or no further reduction in the level of impurities. Vacuum arc melting experiments were therefore suspended.

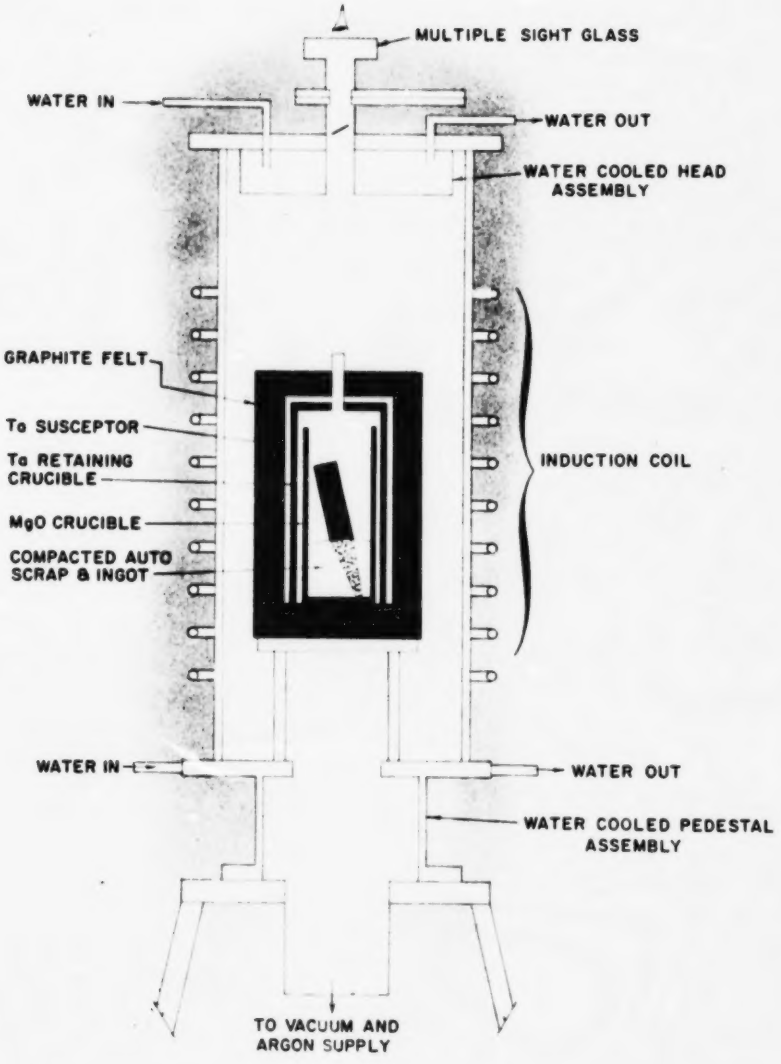
(D) Vacuum Induction Melting (C. V. Owen and J. K. McClusky). Within the past ten years vacuum induction melting (VIM) has become prominent in the production of specialty steels and super alloys,[8]

and consequently this process has assumed a more important role in the steel industry. Two of the advantages of VIM are that both the temperature and pressure of the melt can be adjusted and controlled quite closely during processing. The purpose of this phase of our investigation was to determine what effect varying these two parameters would have on the removal of copper, tin, chromium and nickel from automotive scrap steel during VIM at various retention times. The apparatus used is shown schematically in Figure 10.

(a) Simulated Auto Scrap. For each melt, a 1 kg pressed compact of simulated auto scrap was placed in a MgO crucible measuring 18 cm in height and 4.5 cm inside diameter with 0.32 cm wall. After the compact was loaded in the furnace the system was evacuated and adjusted to the desired pressure. The heating cycle was then initiated during which the pressure was maintained at the desired level. After melting, the resulting ingot was removed from the MgO crucible and a disc 0.6 cm thick was taken at the center and sampled for chemical analyses.

The first series of vacuum induction melts consisted of melting the simulated compacts at 1550, 1650 and 1775°C for retention times of 10, 20 and 40 minutes under a pressure of 1×10^{-3} torr. The data obtained are listed in Table VII (compare with Table II), along with the percent weight loss of each melt. A plot of the impurity concentration vs temperature data is shown graphically in Figure 11.

The increased iron losses at 1775°C appeared to be the result of some chemical reaction occurring in this temperature range. Observations of melts at 1550 and 1650°C showed very smooth flat



VACUUM INDUCTION MELTING OF AUTO SCRAP

Fig. 10 Vacuum induction furnace used to melt auto scrap.

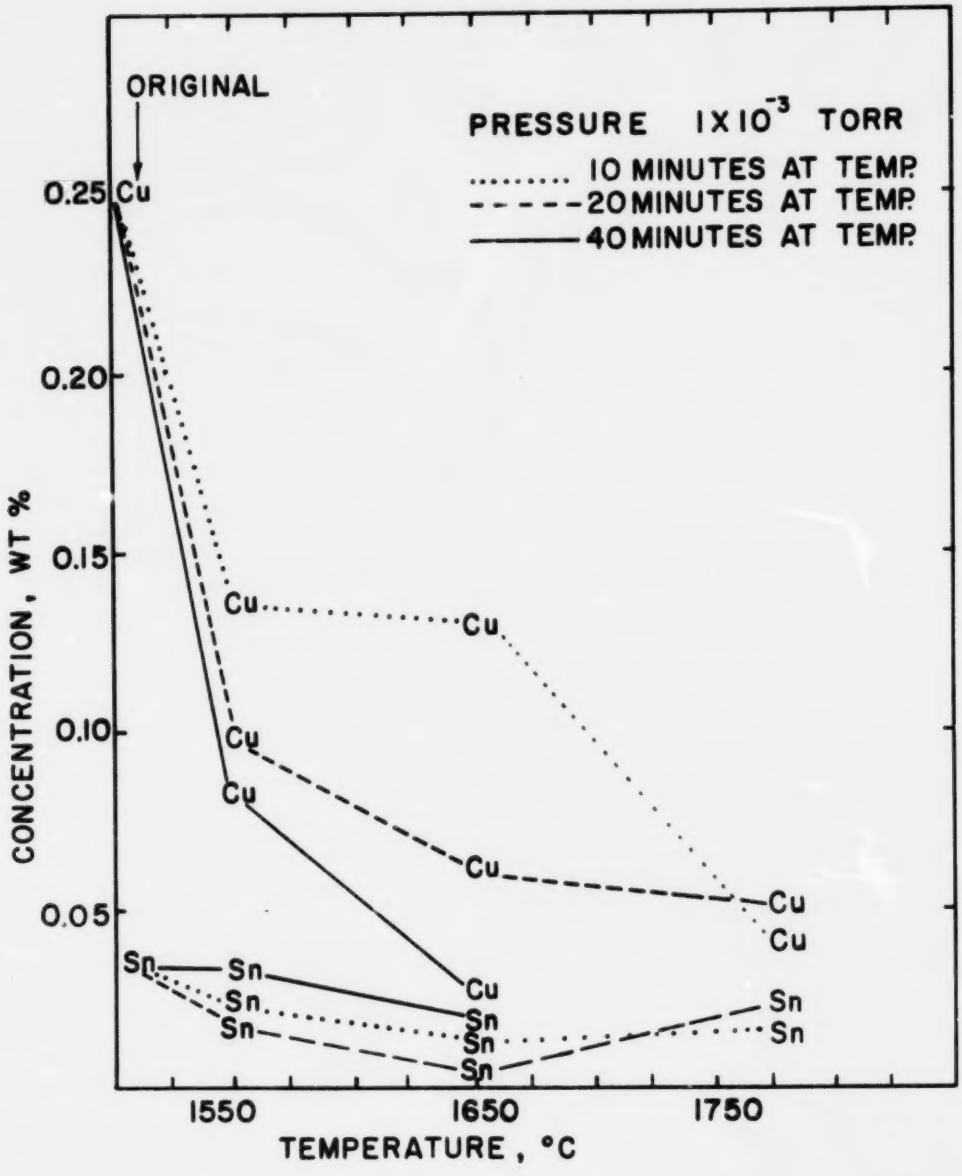


Fig. 11 Impurity concentration vs temperature of vacuum induction melts having various retention times at pressures of 1 x 10^{-3} torr.

Table VII. Analytical Data and Percent Weight Loss of Simulated Auto Scrap Heated at a Pressure of 1 x 10^{-3} torr.

Temp	Time	Concentration, w/o Cu	Sn	Cr	Ni	% wt loss
1550°C	10 min.	0.140	0.023	0.155	0.110	0.5%
	20 min.	0.095	0.019	0.170	0.110	0.9%
	40 min.	0.085	0.032	0.160	0.110	1.5%
1650°C	10 min.	0.130	0.013	0.165	0.110	1.2%
	20 min.	0.060	0.010	0.140	0.110	2.2%
	40 min.	0.027	0.018	0.140	0.110	3.5%
1775°C	10 min.	0.043	0.018	0.150	0.110	4.1%
	20 min.	0.055	0.023	0.120	0.110	11.1%
	40 min.	-	-	-	-	-

liquid surfaces during processing, however at 1775°C the liquid surface would swell periodically and then erupt, splattering liquid metal on the crucible sidewalls. At about the same time in our research efforts similar eruptions were observed during electron beam melting of simulated auto scrap when high superheat temperatures (greater than 1750°C) were used. Residual gas analysis during electron beam melting showed considerable increases in the concentration of gases having amu of 28 and 44. In an effort to better understand this phenomenon high purity electrolytic iron was induction melted in a MgO crucible and superheated to 1775°C under a pressure of 1 x 10^{-3} torr. No eruptions were observed. A small addition of elemental silicon (28 amu) was made and the ingot heated to 1775°C; again, no excessive spattering was observed. In another experiment a small quantity of SiC was added to the electrolytic iron and heated to the same temperature. Shortly after this temperature was attained, the sample began to erupt. A review of the

residual carbon and oxygen concentrations of the processed scrap revealed the melts made at 1775°C were much lower in these constituents than in the samples processed at 1550 and 1650°C. On the basis of the above experiments and the carbon and oxygen data, we believe the loss of metal that occurred at 1775°C was due to the formation and rapid evolution of gaseous CO (28 amu), CO_2 (44 amu) and/or SiO (44 amu). The mechanism for the eruptions is believed to be similar to the "bumping" phenomenon which occurs when liquids containing dissolved gases are heated to high temperatures.

In a second series of experiments the effect of pressure on the removal of copper, tin, chromium and nickel was determined at 1550 and 1650°C. The pressure above the melts was 5×10^{-5} torr which is a factor of 20 lower than the pressure used in the first series of tests. The data obtained are listed in Table VIII and are graphically illustrated in Figure 12.

A review of the copper concentration obtained after processing as shown in Figures 12 and 13 reveals that the residual copper content can be reduced to well below the 0.060 w/o upper limit by processing at either 1650°C for 40 minutes or 1775°C for 10 to 20 minutes at 1×10^{-3} torr. At a pressure of 5×10^{-5} torr, the acceptable upper limit for copper was met after only 10 minutes at 1650°C. Decreases in the tin concentration from 0.035 w/o to 0.010 w/o was obtained after heating for 20 minutes at 1650°C at a pressure of 1×10^{-3} torr. Increasing the processing temperature to 1775°C resulted in an apparent increase in tin concentrations after both 10 and 20 minute retention times. Some of this increase

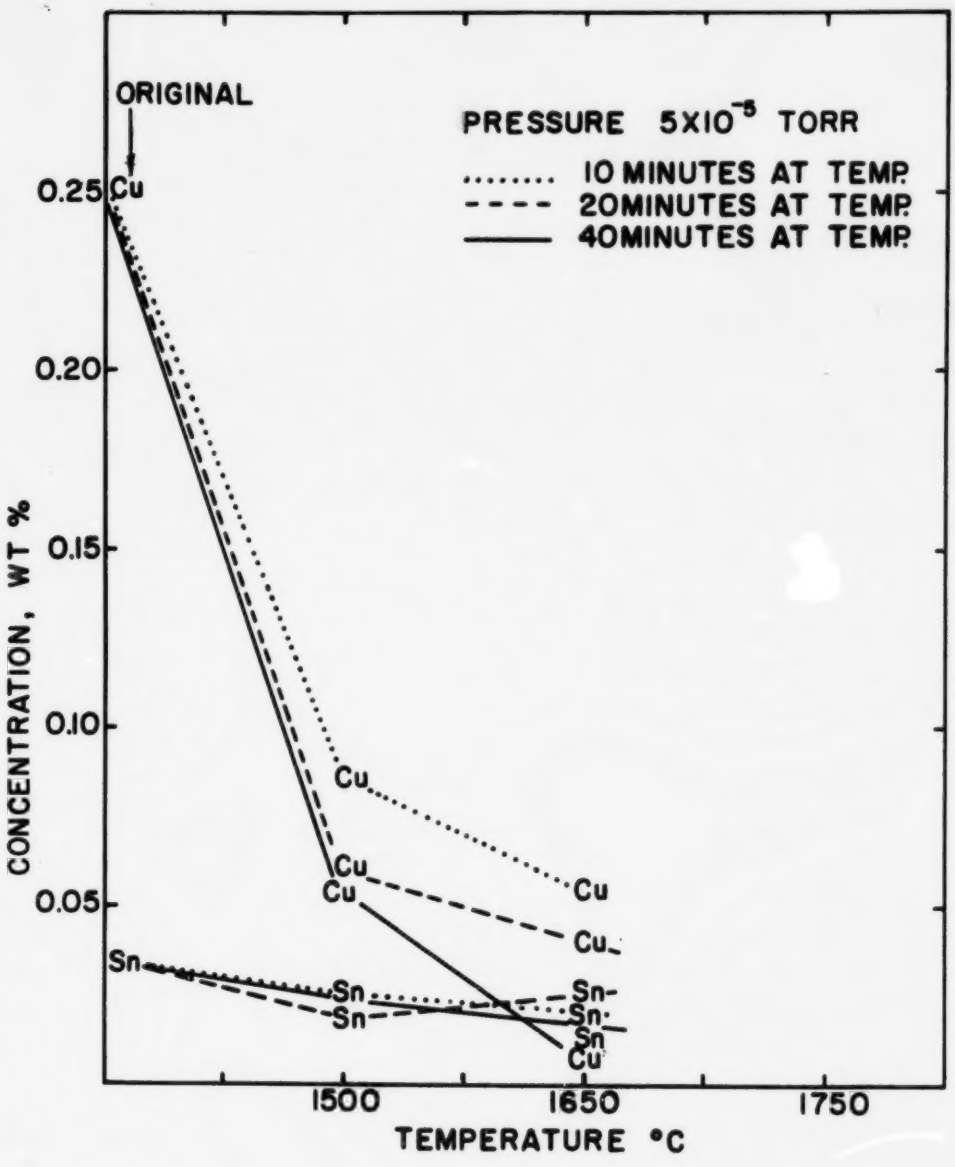


Fig. 12 Impurity concentration vs temperature of vacuum induction melts having various retention times at 5 x 10^{-5} torr.

Table VIII. Analytical Data and Percent Weight Loss of Simulated Auto Scrap Heated at a Pressure of 5×10^{-5} torr

Temp.	Time	Concentration, w/o Cu	Sn	Cr	Ni	% wt loss
1550°C	10 min.	0.085	0.025	0.160	0.110	1.1%
	20 min.	0.065	0.021	0.160	0.110	1.7%
	40 min.	0.062	0.025	0.150	0.110	3.1%
1650°C	10 min.	0.057	0.022	0.160	0.110	2.1%
	20 min.	0.038	0.025	0.160	0.110	3.1%
	40 min.	0.011	0.015	0.140	0.110	6.2%

is due in part to the concentration effect due to iron losses. However, the general fluctuations noted in the tin concentrations are somewhat puzzling and could be a chemical analysis problem.

In a study conducted by Gill et al.[16] on the behavior of various elements in vacuum steelmaking it was reported that initial tin concentrations of 1.76 w/o were reduced to less than 0.010 w/o at 1600°C at a pressure of 1×10^{-3} torr and a 90 minute retention time. Available thermodynamic data on the vapor pressure of tin in liquid iron[15] at 1600°C as well as the results of the present investigation substantiate this observation.

One possible explanation for the rather low removal rates could be the low surface area to volume ratio (0.131) used in all of the experiments. With this in mind, a possible solution to this problem on a larger scale of operation might be to increase this ratio. Such an approach should also enhance the removal of copper.

(b) Preparation of 304 Stainless Steel from Actual Auto Scrap. Our findings that the copper and tin content in simulated auto scrap could be reduced to acceptable levels using controlled vacuum induc-

tion melting (VIM) procedures prompted an investigation to determine the feasibility of converting auto scrap directly into 304 stainless steel. The auto scrap obtained from the Eidal Corporation was used as starting material for this study. Controlled amounts of copper and tin were added to the scrap before melting in order to further verify the removal of these impurities by VIM.

The procedure that was developed for preparing 304 stainless steel from auto scrap consisted of first compacting the scrap containing additions of Fe_2O_3 and nickel. The Fe_2O_3 was added in order to decarburize the iron to a level of 0.08 w/o or less as specified for 304 stainless. The nickel was added as an alloying agent. The compact was then heated to 1650°C under 60 cm of argon pressures for one hour to complete the Fe_2O_3 carbon reaction. The system pressure was then reduced over a period of approximately 30 minutes until the melt was under a vacuum of about 5×10^{-2} torr. This condition was maintained for 20 minutes to insure removal of the copper and tin impurities. During this period the pressure was further decreased to 2×10^{-3} torr. Argon was then readmitted to the system until a pressure of 65 cm of mercury was reached. At this point chromium metal was added and the melt held at 1650°C for 1 hr to insure homogenization of the alloy. Analysis of the resulting ingot showed that copper and tin had been lowered to acceptable levels (Table II) and that the carbon content was less than 0.01 w/o. The chromium and nickel contents were within the range specified for 304 stainless. A typical analysis of this material is shown in Table IX, hence designated as A.L.-S.S.

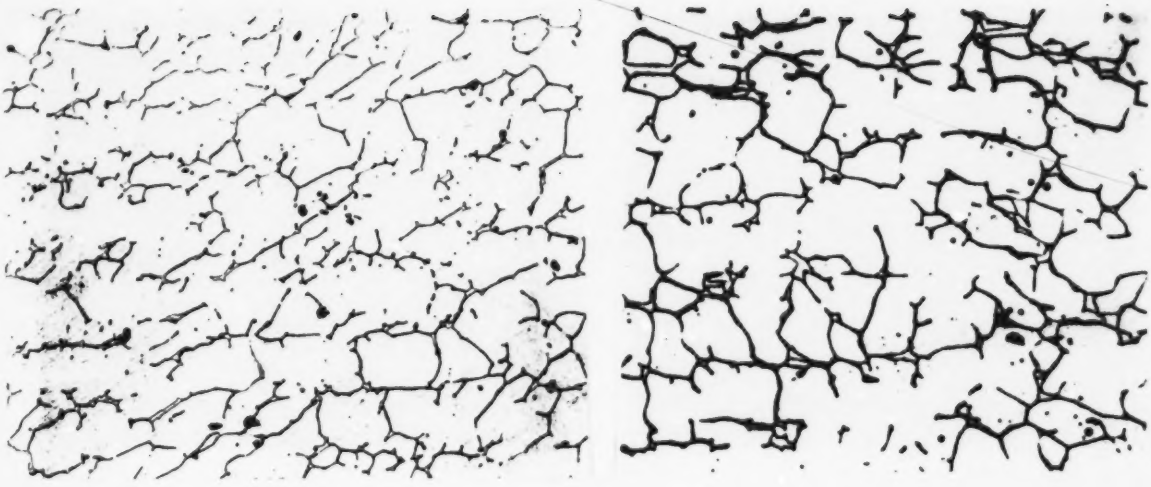
Table IX. Typical Analysis of Stainless Steel Produced from Auto Scrap

C	O	N	Al	Cr	Cu	Mn	Mo	Ni	Si	Sn
.0075	.017	.0018	<.001	19.2	.017	.72	.025	10.0	.03	.002

The very low carbon content of the final ingot indicates that there may be sufficient Fe_2O_3 in the form of rust on the surface of auto scrap to insure adequate removal of carbon but no experimental melts were made to verify this.

Samples prepared from these ingots were evaluated by metallographic examinations and by corrosion testing in H_2SO_4 of varying concentrations. A typical microstructure of the material as cast is depicted in Figure 13 along with a microstructure of CF-3 stainless steel reproduced from the "Atlas of Microstructures of Industrial Alloys." The CF-3 alloy is a 19-10 stainless having a carbon specification of 0.03 w/o maximum. The similarity of the microstructures is very apparent.

For the corrosion testing in H_2SO_4 sheet metal coupons of both commercial stainless steel and A.L.-S.S. were immersed together in the acid solutions. The A.L.-S.S. sheet coupons were prepared by standard rolling procedures used for 304-type stainless steels. Concentrations of 20 v/o, 60 v/o and 97 v/o H_2SO_4 were used in this study. The surface area and weight of each specimen were accurately determined before the test and weight loss measurements were made at approximately one week intervals for one month. The results are summarized in Table X. Corrosion rates for the A.L.-S.S. compared



(a) HNO_3 electrolytic 80X
A.L.-S.S. prepared from actual auto scrap as induction casted.

(b) HCl, HNO_3, acetic acid 100X
CF-3 alloy as cast. Fine network of ferrite (10%) in a matrix of austenite.

Fig. 13 Comparison of typical microstructure of stainless steel produced from actual auto scrap and CF-3 stainless steel.

Table X. Comparative Corrosion Rates for 304 S.S. and A.L.-S.S.

20 v/o H_2SO_4		60 v/o H_2SO_4		97 v/o H_2SO_4	
Sample	Rate $mg/mm^2/mo$	Sample	Rate $mg/mm^2/mo$	Sample	Rate $mg/mm^2/mo$
304	3.1	304	$4.1x10^{-2}$	304	$0.48x10^{-2}$
A.L.-S.S.	3.4	A.L.-S.S.	$3.1x10^{-2}$	A.L.-S.S.	$5.3x10^{-2}$

quite favorably with those obtained for commercial 304 in the 20 v/o solution and exhibits a lower rate in the 60 v/o solution. The A.L.-S.S. shows a significantly higher rate of corrosion than the commercial sample in concentrated (97 v/o) sulfuric acid. These data are shown in Figure 14.

3. Electroslag Remelting (J. K. McClusky, R. R. Lichtenberg and R. E. Shaw).

Electroslag remelting (ESR) is the procedure in which the Joule heating associated with the passage of a current through a molten salt (slag) is used to maintain the salt in the molten state and to melt the material of interest. Several electrode configurations, either consumable or nonconsumable, may be used. In our case a consumable electrode was used. The electrode is melted by the repeated formation of small drops on the end of the electrode, the drops subsequently falling through the slag, agglomerating and solidifying to form an ingot. The molten slag is contained in a water-cooled mold of copper or mild steel. The slag serves as a refining medium for inclusions, and also protects the molten metal from the atmosphere above the melt, thus aiding in the retention of all but the most volatile alloying elements. In addition a small amount of slag solifies on the mold wall, thereby giving a smooth-walled ingot and

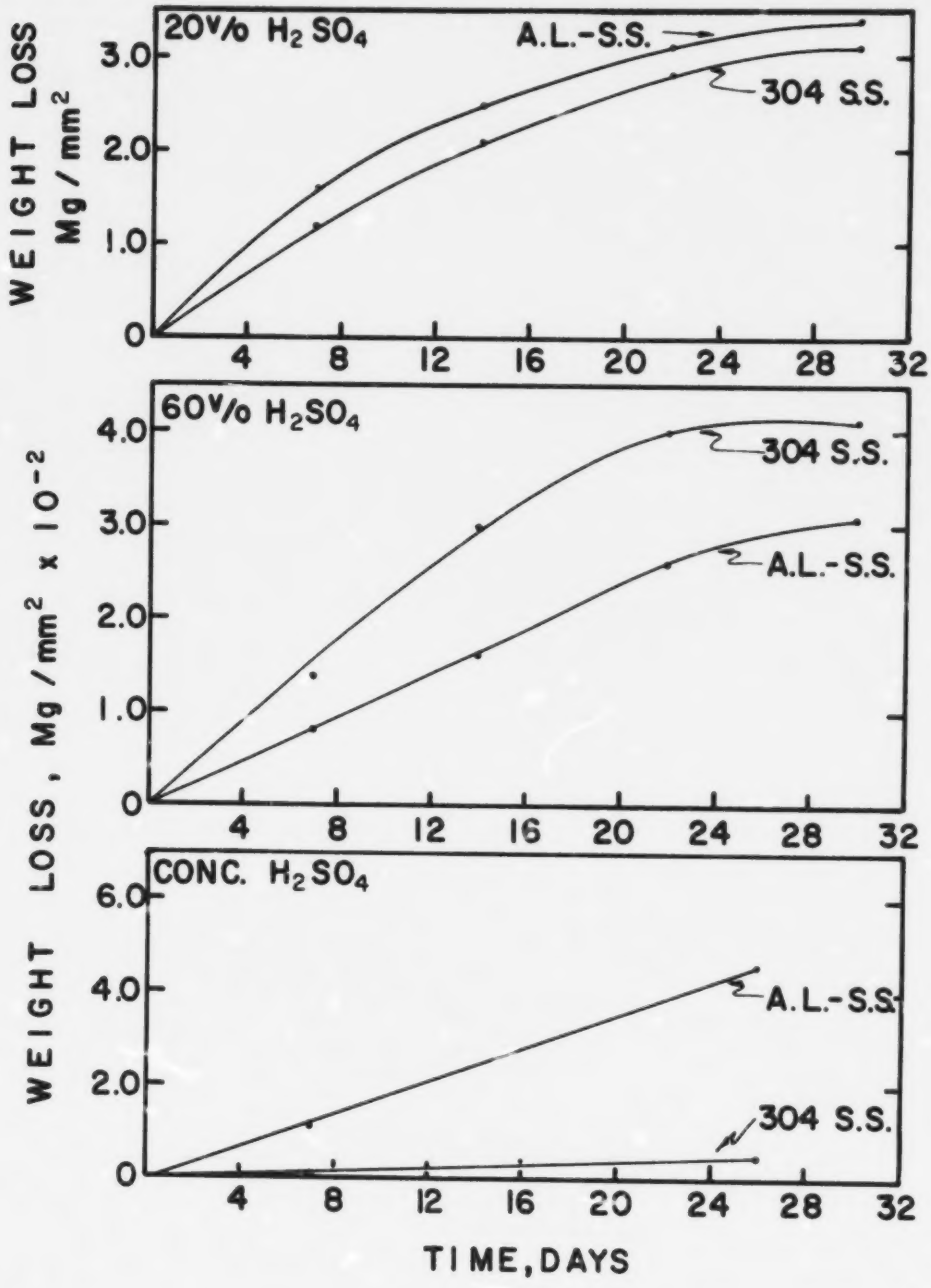


Fig. 14 Corrosion rates of 304 S.S. and A.L.-S.S. in 20 v/o, 60 v/o and concentrated sulfuric acid.

aiding in the direction of ingot solidification. These characteristics are the basis for industrial use of the ESR process.

A question of great practical importance is whether ESR can be used, not to retain metallic impurities in the melt, but rather to extract them. In this proposed application, ESR could be used industrially as a refining process much like electron beam remelting, vacuum-arc remelting, or vacuum induction remelting. The important difference between these different melting methods is that ESR would rely on a refining slag for impurity removal thus obviating the need for a vacuum and the inherent high capital and operating costs of the other refining modes.

Many papers have been written concerning not only the theoretical and experimental aspects of electroslag remelting but also the removal of gases and of oxide, sulfide and other inclusions from electroslag remelted materials. Several excellent review articles are available.[21-26] There is apparently only limited reference to use of ESR as a refining process for metallic impurities. Further, even for those impurities known to be removed, there is no general agreement either to the mechanism or location of the refining action.[22,23,25] Mitchell[24] points out that, in addition to the atmospheric oxidation and inclusion dissolution, there are superimposed electrochemical composition changes due to electrode overpotentials. Whittaker[22] considers a number of types of possible reactions but concludes that several competing effects are present so that a materials balance is not possible. He points out the need for a number of closely-controlled experiments to help

identify the types of reactions taking place.

Whittaker also discusses in detail, for both direct current (dc) and alternating current (ac) cases, the effects of electrode overpotentials superimposed on the chemical potential. Peover[26] concludes that electrochemical reactions in ESR are only secondary to the effect of the heat liberated during the process and its influence on melt rate, equilibrium reactions and operating efficiency. Nevertheless he states that there is a need for much data on the emf and kinetics of electrochemical reactions under the condition of ESR before adequate prediction is possible on the behavior of any system.

Thus it seemed reasonable in our studies of upgrading automotive scrap steel that we include electroslag remelting as a refining procedure. At the outset of this study our Laboratory did not have the capability of electroslag remelting. As a result a substantial amount of our first year's effort was to develop the necessary procedures using conventional slags. Once these procedures were well implemented, research was initiated into finding slags that would serve as extractants for the impurities in simulated auto scrap. The furnace used is shown in Figure 15. Most of the initial melts were made in either a 6.4 or 7.6 cm inside diameter copper mold. Mild steel molds measuring 6.4 cm in diameter were used in later experiments.

Several methods were used to start the electroslag remelting process. The most accepted way of starting is to melt the slag outside the furance and then pour it in with the furnace power on

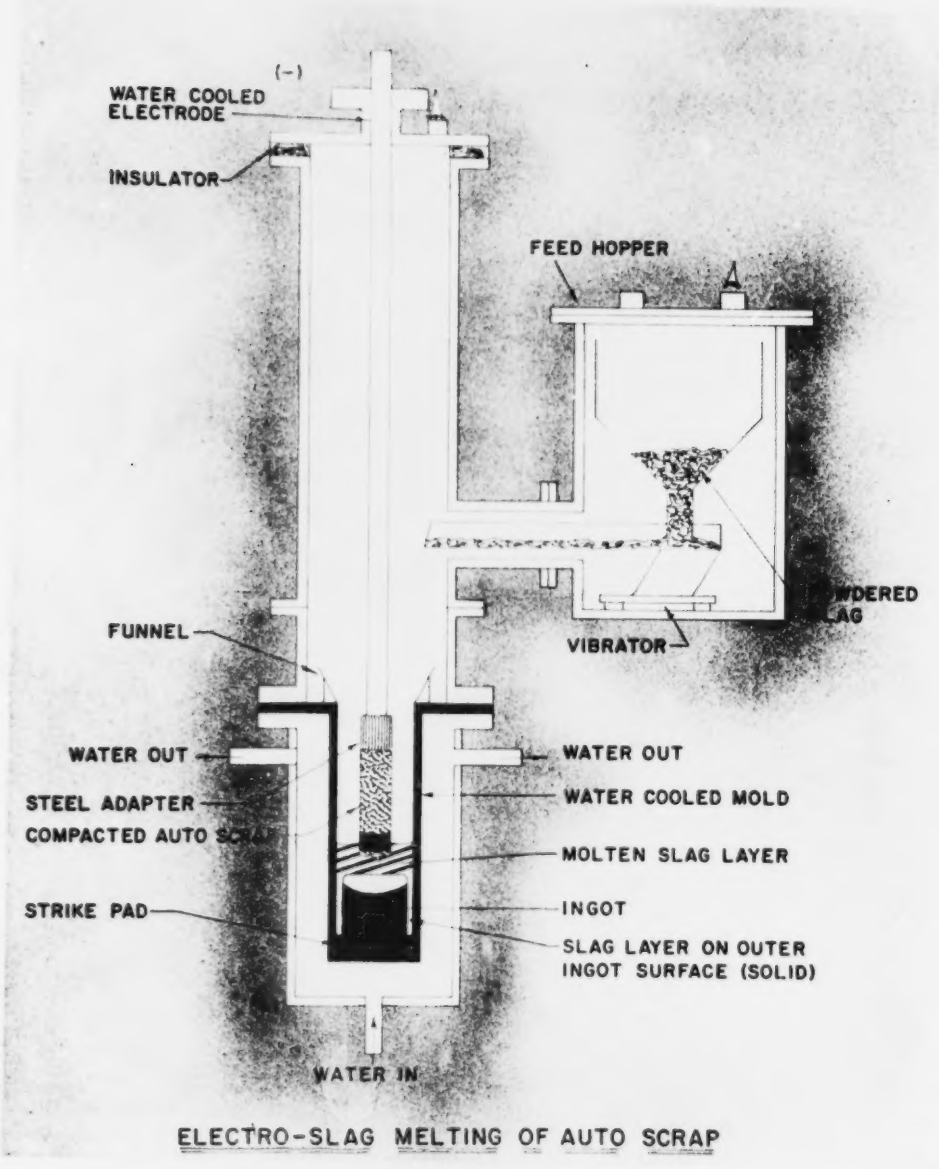


Fig. 15 Furnace used in the electroslag remelting of auto scrap.

and the electrode gap set so that a steady state melting condition is rapidly achieved. This method was not readily adaptable to our apparatus. The starting methods used in this work are described in Table XI. The assigned symbols will be used in later tables describing the results of our refining experiments.

Table XI. ESR Starting Methods

Symbol	Description of Process
ARC	Arc struck between electrode and a loose pile of mild steel turnings surrounded by powdered slag.
S	Starter button which conducts in solid state; 50 or 100 g of composition 34% CaF_2, 16% CaO, 8% SiO_2, 42% TiO_2.
b	Biscuit containing 18 g mild steel turnings and 52 g 75% CaF_2, 25% Al_2O_3; compressed under >2200 kg/cm^2.
b_1	Biscuit conatining 18 g mild steel turnings and 60 g 50% CaF_2, 50% BaF_2; compressed under >2200 kg/cm^2.
b_2	Biscuit containing 18 g mild steel turnings and 75 g BaF_2; compressed under >2200 kg/cm^2.

In general, two types of experiments were performed. An independent slag evaluation study was made on a small scale in an effort to screen various slag systems for copper extraction and for use in the ESR process. At the same time conventional slags with various additions were also being used in the ESR process and the resulting ingot weighing 1 to 2 kg evaluated from surface condition, porosity and chemical analysis.

(A) Independent Slag Evaluation Studies. Because of the large number of possible slag combinations, it was desirable to find an efficient means of evaluating a slag quickly as to its melting point and its reactivity with copper. To do this various copper-

salt mixtures were heated in a crucible by an induction furnace under an argon atmosphere at 1/2 atmosphere of pressure. Included in the testing were various halides, sulfates, sulfides and metallic mixtures.

One of the first compounds tested was iron sulfide because of the relative stability of copper sulfide over iron sulfide. The independent study showed that an iron sulfide containing slag would reduce copper; however, in actual ESR melting, the presence of the sulfide caused unstable melting conditions and very high sulfur levels in the iron.

Various fluorides were used in this evaluation but the fluorides that were stable at high temperatures were also very stable from a free energy viewpoint so that they remained practically inert during the melting operation although they did contribute to the slag's properties by increasing its melting point, fluidity, and electrical conductivity.

The chlorides of magnesium, calcium and barium were also investigated. These chlorides are stable at high temperature and their free energies indicate a possibility of reacting with the metals that are present as impurities in auto scrap. The testing with copper, however, showed very little (<0.5%) copper in the slag phase as was verified by subsequent ESR melts. These experiments did show a reduction in other metallics as described in the next section.

From the work of other investigators it was thought that various sulfates might react with copper as the iron sulfide did,

without adding sulfur to the ingot. Therefore, testing of sodium, potassium, calcium and barium sulfates was initiated. It was found necessary to use a quartz crucible for these experiments since they were reactive to a tantalum or graphite crucible. Unfortunately these compounds again showed little reactivity with copper since very little copper was present in the slag phase.

Since none of the slag studies showed promise of removing copper, attempts were made to add one or more metals which would have a high solubility for copper but would remain immiscible with the iron. The most promising of these metals involved the use of barium metal as the extractant. Five or six grams of barium metal in chunk form was placed in the bottom of a tantalum crucible. The metal was coated by a thin oxide layer. Next about 10 g of powdered slag was added and finally about 3.5 g of copper was placed on top. Slags used included CaF_2; BaF_2; 50% CaF_2, 20% CaO, 30% BaF_2; 20% CaO, 80% BaF_2; 80% BaF_2, 20% BaO. For these studies the crucibles were open at the top. A half atmosphere of argon was used during melting. After melting (typically at 1400 to 1500°C for 5 minutes) the contents consisted of two phases; a metal rich phase at the bottom and walls of the crucible and a slag phase on top. Qualitative analyses showed that in all cases substantial amounts of copper went into the slag phase. These results prompted a series of experiments involving the use of barium metal as an extractant during ESR. Results of the ESR experiments are reported in a later section.

(B) ESR Slag Evaluation Studies. A number of melts were made using a standard ESR slag composed of 65-75% CaF_2, 0-20% CaO, and 10-25% Al_2O_3. The primary purpose of these runs was to study furnace operating characteristics with varying polarity, input power and electrode cross section. The average ingot analysis of eight of these melts (three ac, one dc reverse polarity, and four dc straight or forward polarity) is given in Table XII. The only significant refining action was a reduction in the aluminum content from about 0.06 to 0.0014 w/o. In these eight ESR melts, aluminum was added to "kill" the steel thus eliminating much of the porosity.

Table XII. Ingot Composition in Weight Percent using CaF_2/CaO/Al_2O_3 Slags.

Al	Cr	Cu	Mo	Mn	Ni	Sn	O	N
.0014	.14	.23	.02	.21	.11	.024	.0279	.0030

An analysis of the available free energy data[27] indicate that extraction of copper, tin, chromium or nickel from iron into an oxide slag is quite unlikely since the standard free energies of formation of their oxides are less negative than are those of the oxides suitable for use as slags in ESR. Thus a search was started for a slag system that has refining capabilities and is also suitable for use with the ESR process. For the melting of auto scrap the slag must be stable in the molten state at about 1750°C and must conduct an electric current but still be resistive enough to maintain itself in a molten condition at a temperature sufficient to melt the electrode.

In the following sections, the results using various slags in ESR experiments are given. In describing these results a shorthand system based on that developed by the British has been used.[23] This method of designating slag compositions for the five component system CaF_2-CaO-MgO-Al_2O_3-SiO_2 lists the percent CaF_2 first followed by the suffix F, and oblique stroke, and the percent of other components in order. A zero digit is placed if a component does not appear in a slag, except last zero digits may be omitted. Thus for example 70% CaF-20% CaO-10% Al_2O_3 appears as (70F/20/0/10/0) or more simply (70F/20/0/10). In many of our slags constituents other than the five listed above appeared. They are simply listed at the end of the British notation system with the percentage followed by the compound formula. Thus 45% CaF_2-25% Al_2O_3-30% Na_2SO_4 appears in shorthand as (45F/0/0/25/30 Na_2SO_4).

(a) Chloride Slags. Several chloride slags were investigated and initial experiments were made in a copper mold. During one dc straight polarity run at the 30 kW power level using a (60F/20/10/10 $CaCl_2$) slag considerable attack of the mold occurred. It was postulated that this reaction was due to the oxidation of the mold by the chloride ion present at the mold-slag interface resulting from a concentration build up of these negative ions as a result of the polarity of the system. If this is correct, the mold attack should be substantially lowered or even eliminated if the polarity is reversed and the attack should occur harmlessly at the melt stock that serves as the cathode. A new melt, using a similar slag composition and power level but using reverse polarity, was successful with no attack of the mold occurring.

Unfortunately, analytical results obtained on ingots remelted under reverse polarity with a slag containing 10 w/o $CaCl_2$ revealed that the copper concentrations were essentially unchanged at about 0.25 w/o. As shown in Table XIII there were some reductions in chromium to as low as .08 w/o, tin to <.01 w/o, nickel to .09 w/o, and manganese to <.01 w/o. A comparison was made of the effect of polarity on ability to refine. Runs 1-48 vs 1-34, or 1-51 and 1-104 vs 1-32 show that with nearly identical slags reverse polarity dc may be better for chromium, nickel and tin removal. Only one ac chloride melt was made and no significant refining was observed.

Runs 1-51, -89, -90, -91, -92 and -93 were made under similar melt conditions but replacing some of the CaF_2 with $CaCl_2$. These experiments indicate there may be some increased removal of chromium and manganese when the $CaCl_2$ is increased from 5 w/o to 12.5 w/o $CaCl_2$ but increasing its content still higher has little effect. Runs 1-140 and 1-142 show much better chromium and manganese removal than was generally observed for the chloride slags. These were low power melts, the melt rate being 1/3 to 1/2 that of other chloride melts. The longer slag/metal contact time was apparently responsible for the increased refining. The two melts were started with the TiO_2-containing starter, but there is no evidence that the TiO_2 acted as a refiner.

We must conclude that a chloride-containing slag is not a suitable refining slag overall. The addition of more than about 15 w/o chloride leads to process control problems; the slag tends to splatter on the mold walls and the process voltage is unstable.

Table XIII. Electroslag Melts Made with Chloride Slags

Run	Start	Polarity	Slag Composition	Grams Chloride	Ingot Composition, wt % Al	Cr	Cu	Mn	Ni	Sn	O	N
1-93	Arc	rev	(40F/20/0/10/30$CaCl_2$)	150	.001	.093	.22	.10	.095	.03	.0400	.0021
1-92	↓	↓	(45F/20/0/10/25$CaCl_2$)	125	.001	.095	.23	.12	.10	.04	.0274	.0037
1-108	S	↓	(60F/0/0/10/30$CaCl_2$)	120	.001	.12	.25	.11	.10	.045	.0176	.0032
1-106	↓	↓	(55F/10/0/10/25$CaCl_2$)	100	.002	.11	.24	.09	.098	.042	.0330	.0020
1-149	↓	↓	(55F/10/0/10/25$CaCl_2$)	100	.002	.10	.24	.05	.11	.052	.0176	.0039
1-91	Arc	↓	(50F/20/0/10/20$CaCl_2$)	100	.001	.10	.22	.12	.10	.04	.0390	.0038
2-7	b	ac	(60F/5/0/20/15$CaCl_2$)	82.8	.002	.15	.22	.25	.11	.028	.0217	.0026
1-90	Arc	rev	(55F/20/0/10/15$CaCl_2$	75	.001	.10	.24	.12	.10	.03	.0358	.0034
1-89	↓	↓	(57.5F/20/0/10/12.5$CaCl_2$)	62.5	.002	.06	.26	.10	.10	.027	.0413	.0032
1-105	S	↓	(55F/20/0/10/15$CaCl_2$)	60	.002	.095	.23	.14	.10	.04	.0367	.0017
1-140	↓	↓	(65F/10/0/10/15$CaCl_2$)	60	.002	.053	.26	.30	.12	.054	.0338	.0029
1-50	Arc	↓	(60F/20/0/10/10$CaCl_2$)	60	<.001	.07	.20	.09	.08	<.01	.0350	.0023
1-48	↓	↓	(60F/20/0/10/10$CaCl_2$)	60	<.001	.09	.20	.14	.095	<.01	.0317	.0035
1-53	↓	↓	(62.5F/20/0/10/7.5$CaCl_2$)	52.5	.001	.078	.22	.10	.10	.037	.0361	.0036
1-52	↓	↓	(62.5F/20/0/10/7.5$CaCl_2$)	52.5	.001	.098	.22	.13	.09	.035	.0339	.0024
1-34	↓	for	(60F/20/0/10/10$CaCl_2$)	50	.002	.11	a	.11	.10	.04	.0230	.0030
1-51	↓	rev	(65F/20/0/10/5$CaCl_2$)	30	<.001	.13	.23	.13	.09	.019	.0215	.0031
1-32	↓	for	(65F/20/0/10/5$CaCl_2$)	25	.002	.36	.24	.20	.13	.05	.0330	.0037
1-104	S	rev	(65F/20/0/10/5$CaCl_2$)	20	.001	.12	.23	.13	.10	.04	.0320	.0021
2-9	b	ac	(60F/5/0/20/15$MgCl_2$)	82.5	.010	.16	.24	.22	.11	.023	.0215	.0027
1-142	S	rev	(65F/10/0/10/15$MgCl_2$)	60	.002	.042	.25	.021	.12	.017	.0515	.0026
1-112	↓	↓	(60F/15/0/10/15$MgCl_2$)	60	<.001	.10	.25	.08	.10	.039	.0298	.0017
1-111	↓	↓	(65F/20/0/10/5$MgCl_2$)	20	.007	.11	.22	.12	.10	.039	.0288	.0021
1-95	Arc	rev	(60F/20/0/10/10NaCl)	50	<.001	.10	.24	.15	.10	.03	.0335	.0023

a Significant attack on the copper mold occurred during run 1-34. This apparently resulted in Cu segregation within the ingot

The latter condition leads to fluctuations in the melt temperature. Additions of 15 w/o or less chloride to the slag, however, does result in partial removal of the aluminum, chromium and tin.

(b) Sulfide and Sulfate Slags: Several studies have been made concerning the extractability of copper in the presence of a sulfide or sulfate. A study of the reduction of copper content in molten Fe-Cu-C alloys showed a definite reduction in copper in all heats made.[28] In melts made in graphite molds in an induction furnace the copper content was reduced from 1/8 to 1/2 of the original, and sulfur was reduced by about an order of magnitude. Makar et al.[29] studied the effectiveness of sodium sulfate (Na_2SO_4) in removing copper from both molten iron and actual auto scrap. Apparently the sulfate is first reduced to sulfide. The procedure was to melt the iron in a graphite crucible and then pour the appropriate amount of Na_2SO_4 powder onto the molten metal surface. Additions of Na_2SO_4 ranging from 2.9 to 43.8% gave copper removals of 3.3 to 74.5%. However prolonged holding at high temperatures either caused lower removal efficiencies or removal of copper was generally accompanied by addition of sulfur. Manganese and silicon contents were also substantially lowered but, as with sulfur, showed reversion tendencies at high temperatures and long holding times.

Makar and Dunning[30] carried out a number of other studies including use of sulfate mixtures, recycling of used slags, and a study of the efficiency of lump vs powder slag additions. In 1971, Makar et al.[31] used lance injection to introduce Na_2SO_4 below the metal surface. Several benefits resulted from his work; copper

removal was more efficient, fuming was reduced, sulfur, lead, manganese and silicon were also removed and co-injection of $FeCl_2$ yielded some tin removal. They also found that by withdrawing the slag and lancing it with oxygen or air, Na_2SO_4 could be regenerated and was immiscible with the remaining metal sulfides.

Safiah and Sale[32] have recently pointed out that the previous investigations were carried out on high-carbon or carbon-saturated iron melts. The removal of copper from auto scrap requires a process which works in low-carbon melts. Results from their melts made in an induction furnace on 0.01 w/o, 2 w/o and carbon-saturated melts showed that only in the latter case was substantial copper removal attained with Na_2SO_4 slag. The melt containing 2 w/o carbon showed about a 20% reduction in copper and the 0.01 w/o carbon melt showed less than 10% reduction in copper. These results were explained by the relative activities of copper in the various iron solutions. It was also observed that in contrast to earlier results with high-carbon melts, sulfur pickup occurred when the initial sulfur content was low. This fact along with the volatilization of sodium required to maintain electro-neutrality of the slag were said to limit the use of sodium sulfide slags by steelmakers.

It was believed, however, that ESR might overcome these objections to the use of sulfate containing slags. The possibility of electrochemical reactions during ESR could result in the removal of copper from low-carbon melts similar to auto scrap.

The results of a number of ESR melts made with sulfate-containing slags are shown in Table XIV. No significant reduction in the

Table XIV. Runs with Sulfate Slags

Run	Start	Polarity	Slag Composition	Grams Sulfate	Cr	Cu	Mn	Ni	O	N	C	S
2-38	b	ac	(45/0/0/25/30Na_2SO_4)	165	.025	.22	.08	.10	.076	.061		
2-22	↓	↓	(60F/0/0/20/20Na_2SO_4)	110	.013	.25	.04	.10	.121	.002		
2-28	↓	↓	↓	↓	.09	.28	.04	.09	.028	.002	.092	
2-32	↓	↓	(55F/5/0/20/20Na_2SO_4)	↓	.012	.23	.06	.11	.117	.003		
2-34	↓	↓	(40F/0/0/40/20Na_2SO_4)	↓	.031	.23	.06	.11	.069	.015		
2-36	↓	rev	(50F/10/0/20/20Na_2SO_4)	↓	.022	.26	.05	.11	.090	.055		
2-42	↓	for	↓	↓	.015	.23	.05	.11	.067	.057		
2-50	↓	ac	↓	↓	.011	.18	.06	.12	.082	.035		
1-147	S	rev	(55F/17/0/7/2/8TiO_2/12Na_2SO_4)	60	.031	.24	.03	.11	.068	.003	.010	.211
1-143	↓	↓	(55F/19/0/8/2/8TiO_2/8Na_2SO_4)	40	.026	.26	.03	.11	.054	.003	.008	.216
2-11	b	ac	(67F/0/0/25/8Na_2SO_4)	44	.08	.28	.06	.09	.044	.003		.192
2-44	↓	rev	(67F/5/0/20/8Na_2SO_4)	↓	.047	.23	.04	.11	.039	.023		
2-40	↓	for	↓	↓	.048	.22	.09	.10	.058	.034		
2-48	↓	ac	↓	↓	.011	.24	.04	.10	.060	.053		
1-152	S	rev	(52F/16/0/6/2/8TiO_2/16$CaSO_4$)	80	.014	.24	.03	.12	.097	.005	.007	.357
1-173	↓	ac	(58F/10/0/18/1/4TiO_2/9$CaSO_4$)	50	.043	.24	.05	.11	.060	.002		
2-1	b	↓	(67F/5/0/20/8$CaSO_4$)	44	.063	.23	.06	.11	.061	.002		
1-150	S	rev	(57F/18/0/7/2/8TiO_2/8$CaSO_4$)	40	.052	.25	.04	.12	.052	.006	.010	.168
1-154	↓	↓	(56F/17/0/7/1/7TiO_2/13$CaSO_4$)	38	.014	.25	.04	.12	.092	.005	.007	.210
2-3	b	ac	(67F/5/0/20/8$MgSO_4$)	44	.036	.23	.05	.11	.068	.003		
1-157	S	rev	(62F/18/0/8/1/6TiO_2/4$MgSO_4$)	12	.041	.25	.07	.11	.068	.005	.013	.091
2-5	b	ac	(67F/5/0/20/8K_2SO_4)	44	.095	.24	.08	.11	.043	.003		
2-13	b	ac	(67F/0/0/25/8FeS)	44	.15	.25	.21	.11	.028	.002		.378

copper or nickel content was observed. In repeated experiments the carbon content of the iron was decreased to about 0.01 w/o in the melted ingot. In one experiment 0.5 w/o carbon, in the form of graphite powder contained in a tube, was added to the electrode but the carbon content of the final ingot was only 0.092 w/o. This supports the contention that the carbon reduced the sulfate slag to sodium sulfide and carbon monoxide. We found no reduction in the copper content of low-carbon melts which was in agreement with Safish and Sale.[32] In further agreement with their results substantial amounts of sulfur were found in those ingots that were melted under sulfate slags (see Table XIV). The aluminum content of all these melts was <.003 w/o and the tin content was <0.02 w/o and in most melts <0.01 w/o. It appears that the aluminum, chromium, manganese and tin contents are definitely reduced with ESR, using a partially sulfate slag. The following conclusions may be drawn.

1) With (50F/10/0/20/20Na_2SO_4) or (67F/5/0/20/8Na_2SO_4) slags, chromium removal is most complete when ac melting is employed, then dc (rev) and least when using dc (for). No polarity preference is apparent for the removal of aluminum, manganese and tin.
2) For ac melting with these slags, the 8% sulfate is almost as good as the 20% sulfate slag but for dc melting the 20% slag appears to be better for chromium removal.
3) Comparing the effectiveness of slags of the type (67F/5/0/20/8M_xSO_4) where M is Na, K, Mg or Ca, it is concluded that most efficient removal of metallics occurs with Na followed by Mg, Ca and K. It appears that the oxygen content of the

iron ingot is lowest for K additions followed by Na, Ca and Mg.

(c) Barium Salts and Barium Metal. It is well known that barium and iron are immiscible[33] and that barium is less dense. Since copper is soluble and forms stable compounds with barium, a possible refining method might involve the transfer of copper from iron scrap into a barium-rich phase. In the ESR process, this phase should float ideally on top of the liquid iron pool or dissolve in a molten BaF_2 slag. This, of course, would require that the barium-rich phase be stable under ESR operating conditions and that the barium does not vaporize at the process temperature (around 1750°C) in the prevailing atmosphere.

Table XV gives results from ESR melts made with a slag containing a barium salt both with and without the barium metal addition. The barium was added in the following way. A rod of barium metal was cooled to liquid nitrogen temperature and the outer surface filed clean of oxide. The barium was then carefully swaged to fit into a 0.8 cm inside diameter steel tube. The steel tube was swaged further until an outside diameter of 0.8 cm was obtained. The tube was then crimped about every 2.5 cm to help control the flow of the low melting barium metal during the ESR process. The tube was compacted into the center of a compact of simulated auto scrap which was used as a melt stock in subsequent experiments.

From Table XV it is apparent that during ESR neither barium metal nor barium salts, separately or together, are very effective in removing copper or other metallic impurities from iron. These findings are contrary to those anticipated from the independent slag

Table XV. Summary of Experiments Using Barium Slags and/or Barium Metal

Run	Start	Polarity	Slag Composition	Grams Barium	Ingot Composition Al	Cr	Cu	Mn	Ni	Sn	O	N
2-72	b_1	ac	(4F/78BaF_2/19BaO) Ba[a]	699	.002	.11	.29	.03	.09	<.01	.025	.002
2-76	b_2	↓	(100BaF_2) Ba	638	.08	.16	.28	.04	.11	.02	.012	.002
2-78	↓	↓	(60BaF_2/20BaO/20$BaCl_2$) Ba	630	.002	.14	.22	.05	.10	.01	.013	.002
2-68[b]	b_1	↓	(50F/20/30BaF_2) Ba	218	.025	.31	.29	.36	.13	.02	.017	.003
2-64	↓	↓	(30F/20/50BaF_2)	215	<.001	.15	.25	.27	.12	.02	.021	.002
2-66	↓	↓	(50F/20/30BaF_2) Ba	182	.025	.16	.27	.31	.12	.01	.015	.004
2-62	↓	↓	(50F/20/30BaF_2)	131	.003	.15	.24	.25	.13	<.01	.028	.002
2-59	Arc	↓		129	<.001	.14	.25	.26	.13	<.01	.027	.002
2-56	↓	↓	(80F/20) Ba	50	.005	.15	.24	.29	.12	.01	.014	.003

a The notation Ba after the slag designation means that barium metal was added to the electrode

b This electrode consisted of real auto scrap

studies. A possible explanation for this is that the absence of iron in the solubility studies or else the higher temperatures used in the ESR tests. A mass balance obtained on the slag showed a weight gain corresponding to the amount of barium metal added thus indicating that very little barium was lost by vaporization but rather it had dissolved in the slag.

It is seen from Table XIV that virtually all of the manganese is removed by slags in which the calcium fluoride is replaced by barium salts. It also appears that the nickel content may have been lowered slightly and that aluminum and tin are removed in varying amounts. The oxygen and nitrogen contents of all the melts were quite low. Many of the ingots melted though barium salts showed some porosity. However, no correlation could be made between this property and the amounts of oxygen, nitrogen and barium contained by the ingots.

4. Mechanical Testing (C. V. Owen)

The fabricability of mild steel with high copper and tin contents is effected in two ways. First there is the problem of surface cracking (hot shortness) which can occur during the hot rolling of ingots into sheet and secondly there is the possibility of premature failure of the finished cold rolled sheet during deep drawing or other forming operations. Both of these problems have been investigated in some detail to supplement the purification work and provide adequate evaluation for any purified ingots.

Hot shortness in mild steel containing excessive amounts of copper and tin is caused by the preferential removal of iron from the surface layers by oxidation at the soaking temperature while

the residual elements are left behind in the sub-scale layer in ever-increasing amounts. Given sufficient time at temperature this layer, which is molten, penetrates the grain boundaries at the surface of the ingot causing cracks to open up when the ingot is hot rolled. The presence of cracks on the surface makes the finished sheet steel product unacceptable.

The problem of hot shortness has been studied by various researchers including Melford[34] and Salter.[35] Their findings are reasonably complementary and show that the problem is enhanced by many variables. Basically, however, both Melford and Salter conclude that excessive amounts of copper alone will cause hot shortness and that the presence of tin with the copper is even more detrimental. Both agree that control of the oxygen content of the atmosphere in the soaking furnace can help eliminate the problem. Silver et al.[36] found that sulfur-bearing fuels also contribute to hot shortness of mild steel ingots and stated that they could control the problem by using sulfur free fuels in their soaking furnaces.

Our work in this area consisted of preparing Fe-Cu alloys with varying amounts of copper and soaking samples from each alloy in a furnace for various times at 1100°C. After heating, the oxidized samples were examined macroscopically after the scale was removed and in cross section microscopically for evidence of hot shortness. Indications of hot shortness were observed in all alloys from 9.0 w/o to 0.3 w/o Cu. Only samples containing 0.15 w/o Cu or less remained free of an observable copper-rich surface layer at all soaking times employed. The time necessary to produce copper

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enrichment at the sample surface decreased as the amount of copper in the steel increased. Samples containing more than 0.7 w/o Cu exhibited enrichment after one-half hour while those containing 0.5 and 0.3 w/o Cu required a one hour soaking period. Figure 16 shows this effect of decreasing copper content on the surface of hot rolled mild steel.

The combined effect of copper and tin was also studied and the results were similar to those found by Melford[34] and Salter.[35] In this case alloys containing as little as 0.05 w/o Cu were found to show a copper and tin-rich surface layer when sufficient tin (2.0 w/o) was present. The amount of copper allowable increased with decreasing tin content at equivalent soaking times. The soaking temperature for these samples was again 1100°C. Since our work verified the findings of others, no further work was done in this area.

The problem of accurate laboratory evaluation on the drawing qualities of sheet steel has been considered by numerous investigators. It appears that no single mechanical property adequately describes the formability of a material and consequently parameters such as hardness, yield stress, ultimate tensile strength, yield point elongation, total elongation and uniform elongation have been employed to predict the behavior of materials under production conditions. Small dimensional drawing tests such as the Ericksen cup, Olsen cup, Swift cup and Fukui cup tests[37] have also been used. Some industries use only simulated production forming operations in

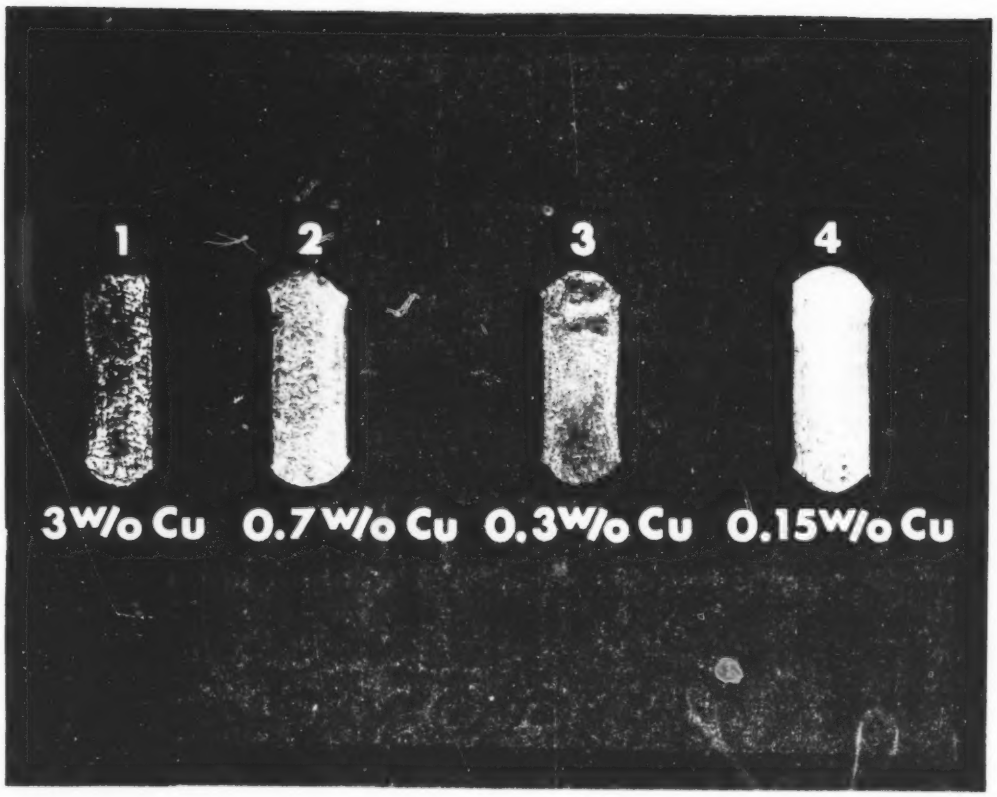

Fig. 16 Effect of decreasing copper content on the surface of hot rolled mild steel. Sample 1 was heated to 1100°C for 1/2 hr before rolling. The other samples were heated for 1 hr.

order to be reasonably sure that a specific material will behave properly under true production conditions. Since none of the above tests will unequivocably predict the forming characteristics of a material, investigators continue to look for more universal parameters.

Recently Keeler[38] wrote a series of articles on this problem which referred to a parameter called the anisotropy ratio, (r),[39] to describe the deep drawing characteristics of a material and suggested that the strain hardening exponent, n, could be employed as an index for a material's ability to undergo stretch forming. He contends that a material with a high anisotropy ratio and high strain hardening exponent can be expected to perform satisfactorily under production forming conditions. The anisotropy ratio is described by the following expression,

$$r = \frac{\ln(Wo/W_f)}{\ln (l_f W_f / l_o W_o)}$$

where l_o and W_o are the original gage length and width respectively and l_f and W_f are the length and width after approximately 0.15 strain. The strain hardening exponent "n" comes from the power equation $\sigma = Ke^n$ where σ is the flow stress and K is a constant of the material. For this investigation both parameters derived from tensile tests and small dimensional drawing tests were used to evaluate the effects of impurities on the formability of mild steel.

Alloys containing copper and tin were made up in compositions ranging from 0.05 to 1.5 w/o. Those for chromium and nickel varied from 0.05 to 5.0 w/o. All alloys were in the form of two hundred gram buttons prepared by melting under purified argon in conventional nonconsumable arc-melting equipment.

The arc-melted ingots were reduced to 0.25 cm thick sheet by rolling at 1100°C, after which the surface scale was removed in a 50 v/o HCl-H_2O solution. The cleaned slabs were further reduced to a final thickness of 0.076 cm by rolling at room temperature. Tensile specimens were cut from the finished sheet at 0, 45 and 90° orientations to the rolling direction in order to obtain a composite picture of the various mechanical properties of interest. After machining to final dimensions each sample was given a final anneal at 750°C. Duplicate tensile tests at each impurity concentration and each sample orientation were performed on a screw driven Instron TT-C tensile machine.

From the data obtained in the tensile tests such mechanical parameters as the anisotropy ratio (r), strain hardening exponent (n), lower yield point (Sy) and ultimate tensile strength (Su) were calculated for each specimen tested. These data were then plotted graphically as a function of the alloy concentration.

The effect of tin, copper, nickel and chromium on the yield strength and ultimate strength is shown in Figure 17. In general all four elements cause an increase in Sy and Su as the alloy concentration is increased, although at low concentrations (<0.7 w/o for copper and >1.5 w/o for nickel and chromium) there appears to be little change. There is an appreciable decrease in Sy at chromium concentrations above 2.0 w/o. This effect has been reported by Edwards et al[40] as well as other investigators. From Edwards data this decrease was calculated to be 3.8 kg/mm^2/w/o between 3 and 6 w/o and is in good agreement with the results of our investigation. The reason for this decrease in Sy has not been satisfactorily explained to date.

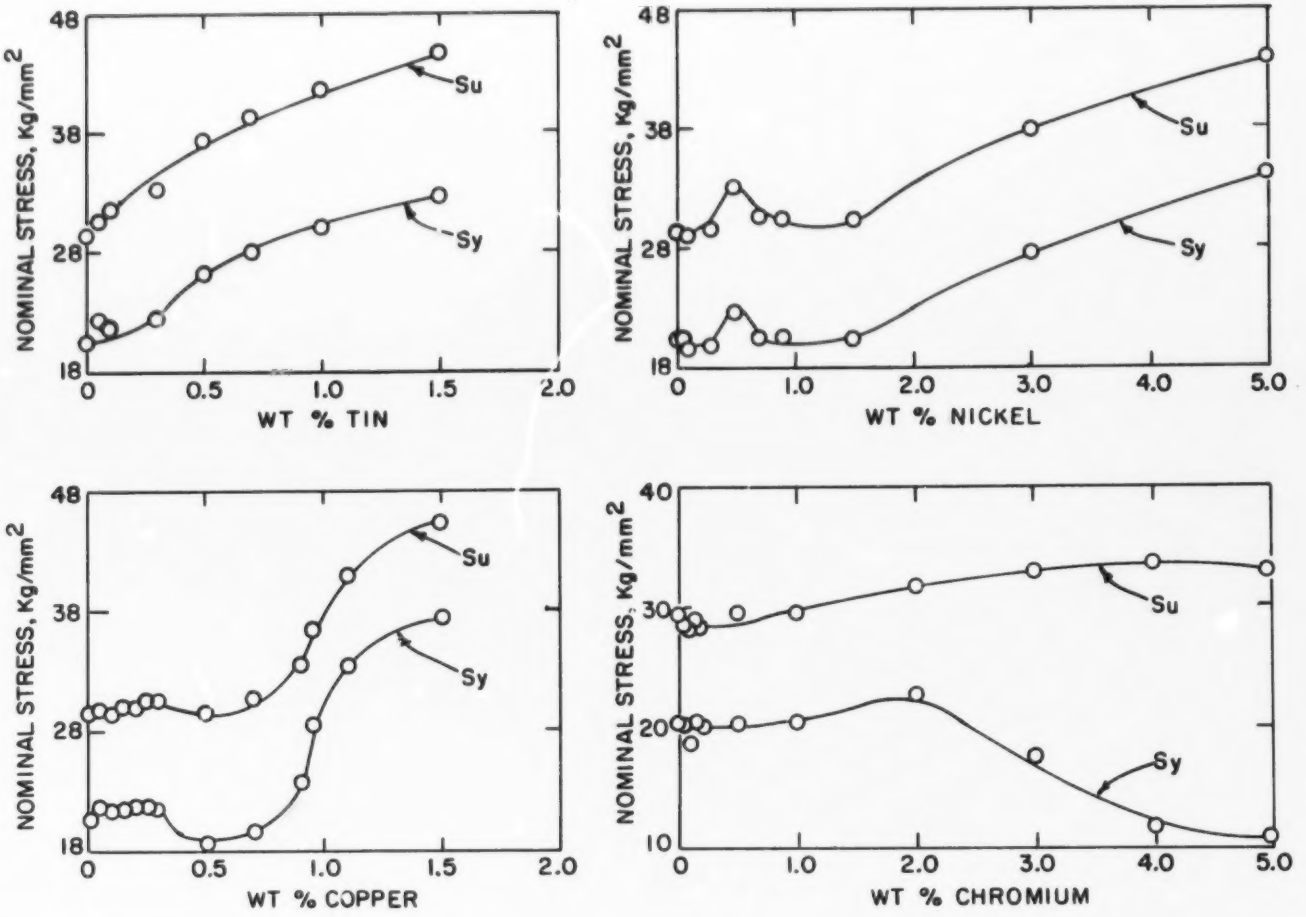

Fig. 17 Effect of tin, copper, nickel and chromium on the yield strength and ultimate strength of mild steel.

In Figure 18 we see the effect of the various alloy additions on the strain hardening exponent. Increases in the tin, copper and nickel contents cause a decrease in this parameter, particularly in the case of copper at concentrations above 0.7 w/o. Chromium on the other hand increases the value of (n) with increasing concentration. As has been stated earlier the strain hardening exponent is considered a good indicator of a material's ability to undergo stretch forming. We would therefore expect additions of tin, copper and nickel to be somewhat detrimental while an increase in chromium content should be beneficial to this forming property.

The normal anisotropy ratio $(\bar{r})^{41}$ is plotted as a function of alloy concentration in Figure 19. This paramater is defined as the expression,

$$\bar{r} = \frac{r_o + 2r_{45} + r_{90}}{4} .$$

There appears to be little or no effect caused by additions of tin up to 0.7 w/o. Above this concentration there is a precipitous drop with increasing alloy content. Copper additions exhibit a converse effect showing minor variations up to 0.5 w/o then a rapid increase in $(\bar{r})$ up to 1.5 w/o. Both nickel and chromium additions show little or no effect on this parameter within the range of alloys tested. "Spikes" have been drawn in the nickel and chromium curves below 0.5 w/o but it is beyond the scope of this investigation to determine if these anomalies are truly significant.

As was the case for strain hardening, formability (in this case ability to be deep drawn) would be expected to increase with

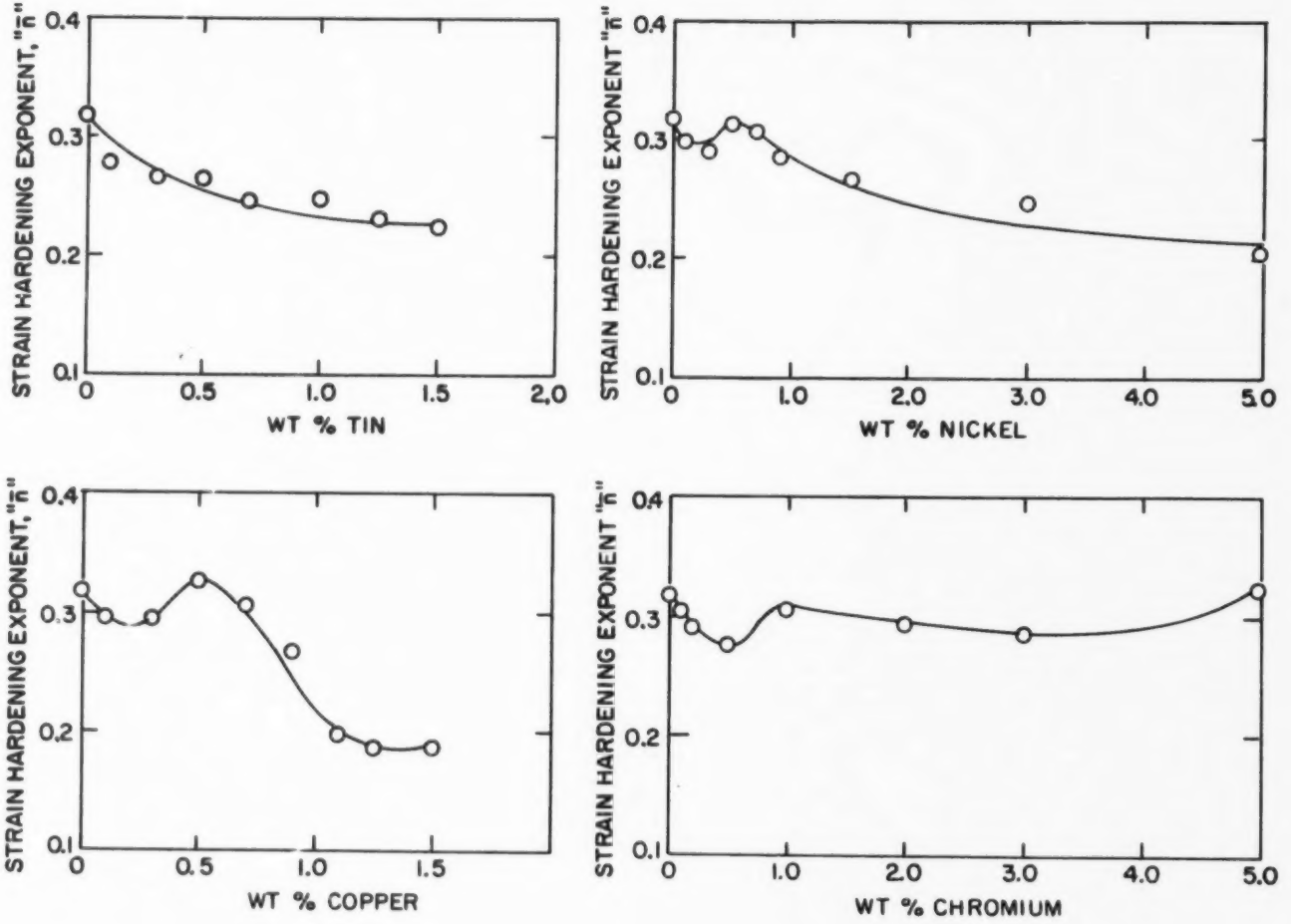

Fig. 18 Effect of tin, copper, nickel and chromium on the strain hardening exponent of mild steel.

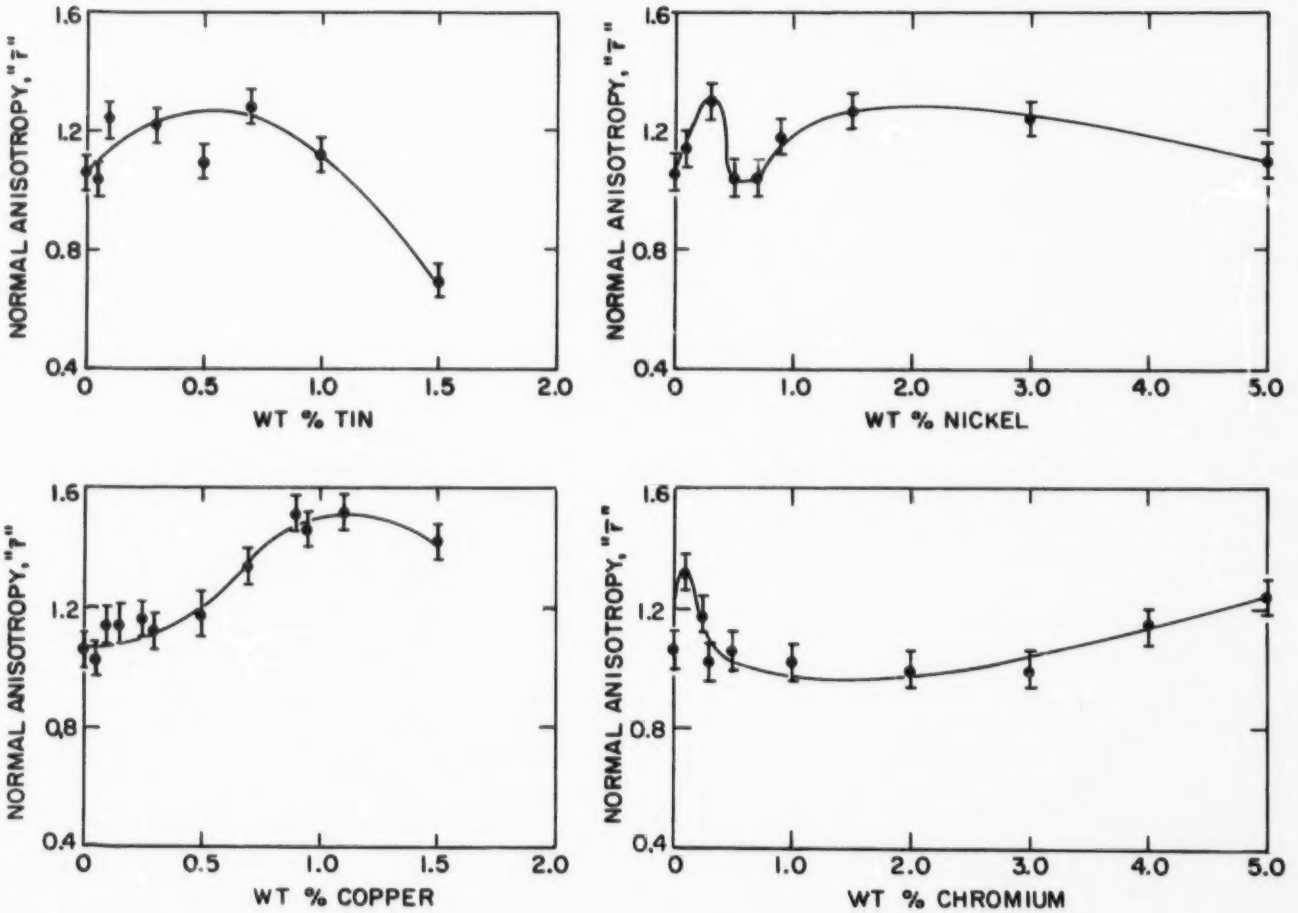

Fig. 19 Effect of tin, copper, nickel and chromium on the normal anisotropy of mild steel.

increasing $\bar{r}$. On the basis of this premise one would predict that tin, in amounts greater than 0.7 w/o, would be detrimental to the ability of steel to undergo deep drawing while copper should improve its drawability at least for the compositions tested. Both nickel and chromium exhibit a less pronounced effect, but in general using $\bar{r}$ as the sole criterion for formability, it appears that nickel additions will cause some slight decrease while chromium should improve the deep drawing properties.

Since the strain hardening coefficient and the anisotropy ratio each indicate a different type of drawing behavior, it becomes somewhat confusing to accurately predict complete formability from either one separately. Lankford[39] found excellent correlation between actual production performance and the product of r and n. Wybo[42] found the $(\bar{r} \times \bar{n})^*$ product to be in good agreement with results from laboratory cup tests. Lankford made his comparison on the basis of 46 lots of fully aluminum-killed low carbon steel while Wybo compared the $(\bar{r} \times \bar{n})$ factor to Fukui cup tests with good results.

These investigations, as well as the proposals in Keeler's article, lead the authors to believe that the $(\bar{r} \times \bar{n})$ parameter gives the most accurate correlation between laboratory tests and actual product press performances. Therefore in Figure 20 $(\bar{r} \times \bar{n})$ has been plotted against alloy concentration. On the basis of these curves one would expect only minor effects from tin additions up to 0.5 w/o, but above this concentration the formability would

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* $\bar{n}$ is described by the expression $\bar{n} = \frac{n_o + 2n_{45} + n_{90}}{4}$

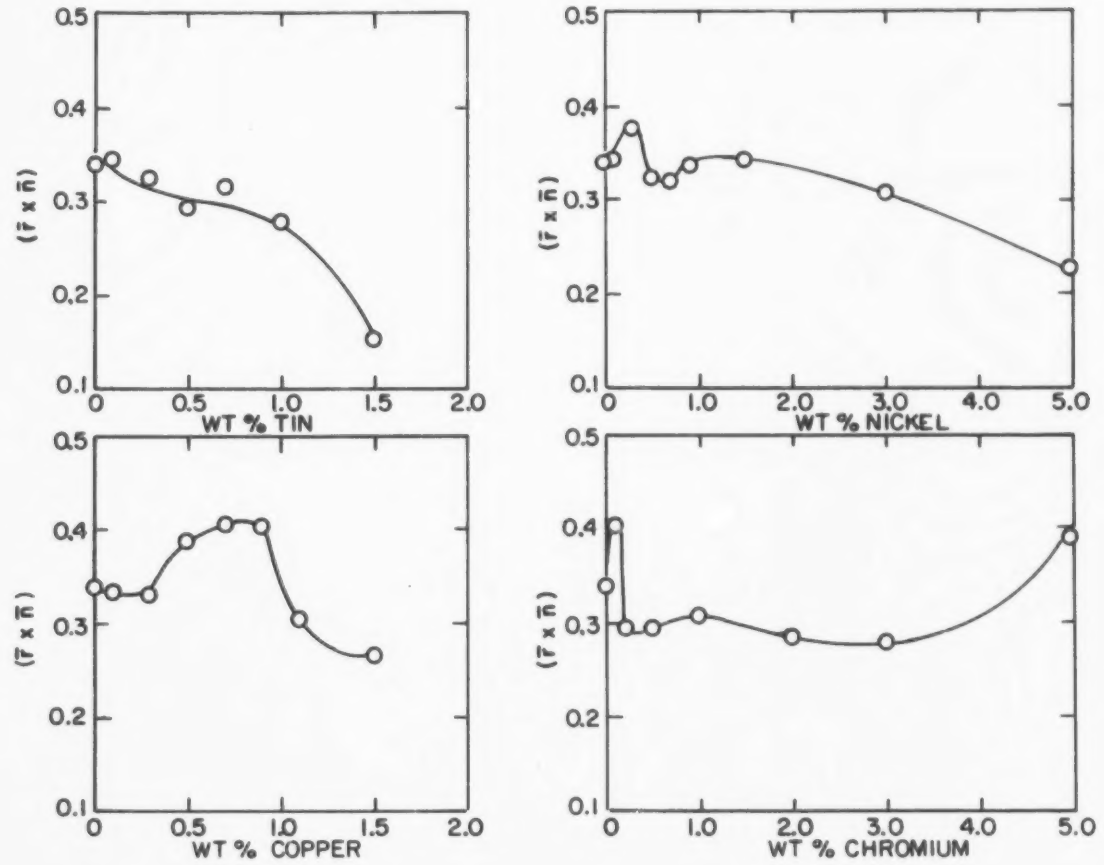

Fig. 20 Effect of tin, copper, nickel and chromium on the product of the normal anisotropy ratio ($\bar{r}$) and the strain hardening exponent ($\bar{n}$) of mild steel.

be seriously degraded. Copper would appear to enhance the formability of steel up to approximately 1.0 w/o followed by a significant drop at higher concentrations. Nickel causes only a slight decrease in drawing performance over the range of alloys tested while chromium has little or no effect up to 3.0 w/o with an indication of improved formability at higher concentrations.

As mentioned at the beginning of this section, some small dimensional drawing tests in the form of Olsen cup tests (stretch forming) and Fukui cup tests (combined behavior) were performed on selected alloys in the series. Although these tests did not show actual failure in any of the alloys, the physical appearance of the specimen in the region of greatest strain agreed qualitatively with $\bar{r} \times \bar{n}$ results. This agreement took the form of an "orange peel" surface condition with noticeable thinning at the areas of greatest curvature.

5. Methods of Chemical Analysis

The change in concentration of impurities in the simulated and actual auto scrap resulting from the various experimental castings was determined by chemical analysis. In each case a center slice was cut from the processed ingot approximately 0.65 cm thick. From this disc six or eight cube samples 0.65 cm on a side were cut. These cubes were surface cleaned by ultrasonic washing using a 10% HCl solution. They were then rinsed in distilled water, dried, and electropolished for 1 minute in a 6% $HClO_4$-CH_3OH solution and sent to our Analytical Service Groups for chemical analysis.

The carbon concentration was determined by the combustion chromatographic method in which the iron sample is ignited in a stream of oxygen gas and carbon as CO_2 is absorbed on a molecular sieve. The gas stream is switched from oxygen to helium and the molecular sieve trap heated to release the CO_2 gas which is passed through a column of silica-gel to separate out water-vapor and other combustion products. The amount of CO_2 is then measured by a thermal conductivity detector.

Prior to analysis for metallic impurities, the samples were dissolved in aqua regia in order to destroy any previous metallurgical history and facilitate the preparetion of standards. These solutions were analyzed by an emission spectrometric technique using a high frequency induction-coupled plasma source for sample excitation.[43] The standards were prepared from Glidden iron solutions to which known amounts of each of the impurities were added. The analysis for oxygen and nitrogen impurities in the samples were performed by a standard vacuum fusion technique using a platinum bath at a temperature of 1580°C. A sample size of 150 mg was optimum for the range of concentrations found in the samples.

DISCUSSION AND CONCLUSION

In this research our object was to determine the critical parameters for a melting-refining process that is both technically and economically feasible. Such a procedure could then be incorporated into a "melt-shop" and combined with a mini-mill steel fabrication plant. In this way auto scrap could be melted, refined and consolidated into ingot form and then fabricated into the desired shapes. By locating the "melt shop" at the same site as the mini-mill operation, good control of the melted product could be obtained and ingot quality varied as required. With this approach the melting, refining and fabrication would all be carried out regionally and, since the auto scrap problem is also regional in nature, larger shops and mills could be established in those areas where the most scrap is available. This concept would tend to minimize shipping costs since some increase in the efficiency of transportation of scrap to the site and fabricated products to their distributors could be realized.

By purifying the auto scrap steel during melting, a continual upgrading of the steel in this country would be accomplished. This is not generally the case in the steel mill or foundry today where scrap is added to the furnace and melted with minimal removal of the more critical impurities. Thus, only a limited quantity of impure scrap can be used before these impurities reach a critical level thereby resulting in a devaluation of the primary product. This procedure results in the accumulation of contaminants in the steel and its continuation would eventually result in the degradation of one of our most important natural resources.

The objective of our work for the first year was to determine the conditions necessary for the removal of copper, tin and chromium from simulated auto scrap steel using various methods of reduced pressure melting. During the second year, actual auto scrap was melted and purified under the most favorable conditions established for the simulated scrap. Also included in this study was an investigation into the potential use of electroslag remelting as a method of consolidating and upgrading auto scrap. This later effort was funded by the Rockefeller Foundation during the first year and work was continued for the 1972-73 period under the EPA grant. In the following paragraphs the various methods used for purification of auto scrap are evaluated.

(a) Nonconsumable Arc Melting. Our small scale experiments showed that none of the impurities found in shredded auto hulks, with the possible exception of manganese, can be removed by this process. When a nonconsumable electrode is used in our melting furnaces the pressure over the melt must be at least 0.64 cm of argon or helium gas in order to sustain the arc. Even with high super-heats of the melt no decrease in the impurity concentration was obtained except for the manganese. The use of this type of melting for the purification of auto scrap therefore does not appear to be feasible unless lower pressures can be used.

(b) Electron Beam Melting. The electron beam melting of simulated and actual auto scrap has been successful in decreasing the copper, tin and chromium to acceptable levels. Copper and tin may be removed in the presence or absence of carbon in the melt.

Because of the formation of stable chromium carbides, chromium could not be removed by volatilization unless there is sufficient oxide present for carbon removal. The manganese and nitrogen concentrations were also substantially decreased to less than 0.04 w/o. The concentration of nickel was lowered in the actual scrap when excess oxygen was present but this decrease was unpredictable, being as high as 60% in some experiments while in others only 10% of the nickel was removed. The addition of various chlorides and fluorides to the melt of simulated scrap resulted in no significant removal of chromium or nickel. The copper and tin concentrations, however, were decreased as usual in these experiments.

Highest metal yields were obtained when a small amount of aluminum wire was added to the compacts of actual auto scrap prior to electron beam melting. The aluminum served to "kill" the melt and significantly decrease the violent evolution of CO and CO_2 which caused excessive splattering and low melt yields. The addition of aluminum was also found to be quite advantageous in those melts in which excess oxygen was added in the form of Fe_2O_3 in order to lower the chromium and nickel contents. The addition of aluminum and Fe_2O_3 may seem superfluous since one would think the aluminum would simply reduce the Fe_2O_3. However when both of these materials were added to the compacts of actual auto scrap metal, yields of 80% were realized and the copper, tin and chromium were substantially lowered in a single melt. The exact mechanism of this behavior is not understood but it does appear that the CO

from the carbon-Fe_2O_3 reaction and the chromium carbide-Fe_2O_3 reaction is less vigorous when a small amount of aluminum is present.

A 7.6-cm diameter ingot of actual auto scrap was electron beam melted and, from chemical analysis, it was found to have the same concentration of impurities as the smaller melts. Both aluminum wire and Fe_2O_3 were also added to the melt in order to insure the removal of copper, tin and chromium to acceptable (Table II) concentrations with good metal yields. It was hoped during this study that several large ingots (15 to 20 cm in diameter) could have been prepared by commercial melters using the conditions developed in our study. This part of our objective was not accomplished due to the extended time that was needed to develop the optimum conditions for impurity removal.

The cost of commercial scale electron beam melting in a 300 kilowatt furnace is approximately 8 to 10 cents per pound ($160 to $200 per ton). In a 1.5 megawatt furnace for some metals it is as low as 5 cents per pound ($100 per ton). However large scale electron beam melting is still in the early stages of development and cost projections by members of the industry on a 500,000 ton/yr volume are in the range of $30 to $60 per ton. The use of electron beam melting, as with any electrical melting method, may become more attractive in the future if a significant supply of low-cost off-peak electrical power becomes available through the development of more efficient power stations such as those developed around nuclear reactors.

(c) Vacuum Arc Melting. The consumable electrode vacuum arc melting of simulated auto scrap was not developed into an effective method of removing impurities. Vacuum arc melting is a difficult procedure on a small scale (2.5 to 5 cm diameter ingots) since cooling rates are quite high and the volume of volatile metal ions is small. Our efforts using a 7.5-cm diameter mold, increased pumping capacity, and improved power control and electrode drive features did not result in slower melting rates which we feel are necessary in order to achieve purification of copper, tin and chromium by this method. We believe that the full potential of this method has not been demonstrated and the successful removal of these impurities may yet be achieved if auto scrap is melted in large furnaces. It should be mentioned that plasma-arc melting was not included in this study. This type of melting has several features that lend themselves to the successful removal of impurities from auto and other types of metal scrap.

Vacuum arc melting is an accepted commercial process in the U.S. and, depending on whether one or two melts are required, cost figures of 3 or 6 cents per pound ($60 or 120 per ton) have been obtained from large-scale operators. Since prolonged retention times in the molten state can be better achieved on large castings, this method of impurity removal should become more efficient as the size of the melt is increased.

(d) Vacuum Induction Melting. This type of melting on a large commercial scale is the most expensive of the methods studied. Costs usually run from 8 to 14 cents per pound or $160 to $280 per ton. Our experimental studies have shown that elemental

copper and tin can be effectively removed from both simulated and actual auto scrap using realistic processing temperatures, pressures and retention times. Decreases in the manganese, oxygen and carbon content are also realized and overall ingot yields of 96% or better are achieved. Even better purification efficiency would be expected using a crucible that affords a more suitable surface to volume ratio.

Vacuum induction melting was also successfully used to remove chromium from actual auto scrap. The procedure used was similar to that employed using the electron beam furnace in which Fe_2O_3 was added to the melt to react with the stable chromium carbide thus forming volatile chromium metal and carbon monoxide.

A procedure using vacuum induction melting was developed whereby a high quality grade of 304 stainless steel can be prepared from actual auto scrap. In this method the scrap is first heated under vacuum to remove the copper and tin. The pressure is then raised and sufficient chromium and nickel are added to increase these concentrations to 18% chromium and 8% nickel. The resulting steel compares favorably with that which is available commercially. It is low in carbon content, and has a very good corrosion resistance to sulfuric acid.

Vacuum induction melting is widely used industrially in the preparation of specialty steels. The demand for these steels is presently quite small as compared to mild steel usage but because of our societies ever increasing demand for structurally superior materials, their utilization will certainly increase. The use of scrap metal as a starting product for these speciality steels could readily defray some of the high cost of this type of melting.

(e) Electroslag Remelting. Although a single all-purpose slag was not found that could be used to remove copper, tin and chromium from auto scrap, we believe electroslag remelting has a tremendous potential for the upgrading of all types of scrap metals. When we used slags containing 10 w/o $CaCl_2$, the aluminum concentration was decreased to <0.001 w/o, the chromium to 0.07 to 0.09 w/o and the tin to <0.01 w/o. Even better removals of these elements and manganese were achieved using a slag that contains some sulfate. It appears that substantial removal may occur with 8% sulfate or less. A viable scheme would have to overcome the problem of high sulfur content in the ingots. If the amount of sulfate required can be minimized, a proper slag addition may serve to refine the sulfur. Of course, this problem does not exist when chloride slags are used.

Sufficient time was not available to fully explore the use of barium salts in the ESR slags as extractants for impurity elements, especially copper. From the small scale independent slag studies some extraction of copper into slags containing barium ions was achieved. Additional studies utilizing this approach should be made.

The removal of aluminum and tin from steel using ESR may be quite desirable as a method of removing these elements from aluminum top beverage cans and from so-called tin cans. Additional studies should also be made in this area as well as using ESR to extract selected metal fractions from municipal refuse.

The cost of large scale ESR is placed at 3 to 4 cents per pound or $60 to $80 per ton, similar to a single vacuum arc melt. Additional economy in melting costs could be realized using iron

molds in place of the usual copper molds. Electroslag remelting is usually used by the casting industry to keep certain alloying elements in the melt in order to enhance the metal's properties. Our use of it as a purification method by extracting impurities from the melt into the slag layer could possibly lead to an expanded process of metal recycling.

At the beginning of this project is was reported in the literature that copper and tin cause hot-shortness in steel during the rolling process. This fact was confirmed by our mechanical testing studies and only samples containing 0.15 w/o Cu or less remained free of a copper-rich surface layer at all soaking times employed. The combined effect of copper and tin was also studied and alloys containing as little as 0.05 w/o Cu were found to show a copper and tin-rich surface layer when tin was present in amounts of 2 w/o or more.

Chromium does not cause hot-shortness in steel but was reported to suppress its ability to be deep drawn. Our results, based on the product of the strain hardening exponent and the anisotropy ratio, do not support this adverse effect of chromium on the formability of steel but rather indicate a slight enhancement. Tin and copper likewise appear to have no detrimental effect on the formability of steel when present in low concentrations (0.5 to 1 w/o) but show evidence of degrading its formability at higher concentrations. A slight decrease in drawing performance is observed in alloys containing up to 5 w/o nickel.

RECOMMENDATIONS

This project was limited to the laboratory study and development of a method for purifying simulated and actual auto scrap by several melting techniques. Our recommendations concerning future work on this problem are as follows:

1. The purification of automotive scrap steel by non-consumable arc melting does not appear to be feasible unless the pressure over the melt can be maintained at 1×10^{-3} to 1×10^{-4} torr. We could not achieve these conditions in our small furnaces; however, large commercial processes like the Durarc Process developed by the Westinghouse Corporation have this capability. In this type of melting a 10 to 12 cm diameter water-cooled electrode is used and the pressure over the melt can be varied from 5×10^{-4} to 4×10^{2} torr.

2. Automotive scrap steel can be purified of copper, tin and chromium to acceptable levels (Table II) by electron beam melting. In order to remove chromium, low concentrations of carbon must be present. Electron beam melting is now quite expensive; however, it may become more attractive in the future if a significant supply of low cost off-peak electrical power becomes available. We recommend that several large melts 12 to 15 cm in diameter of auto scrap be made by industry using the conditions determined during our investigation. The resulting ingots should be evaluated in a mini-mill fabrication operation so that

more process variables could be studied and a good cost analysis made.

3. We were unable to purify either simulated or actual auto scrap by vacuum arc melting. However, we recommend that larger melts in industrial furnaces should be attempted before this type of melting is ruled out. In such units, longer retention times in the molten state and larger diameter ingots with more surface area can be made. Both of these conditions should enhance impurity removal.

4. Copper, tin and chromium can also be removed from auto scrap by vacuum induction melting. In the present study we developed a one step process for preparing 304 stainless steel from auto scrap in a single heating step. We recommend that further studies using this type of melting be directed toward the preparation of speciality steels from auto scrap.

5. We believe electroslag remelting (ESR) has the greatest potential of any of the melting methods studied for scrap metal consolidation and purification. The cost of ESR is competitive with present melting operations and the use of the slag layer as an extractant media for impurities has tremendous refining possibilities. In our work we did not find a slag mixture that would remove copper from auto scrap. Since we were successful in removing aluminum, chromium and tin from scrap steel by this method, we recommend that further studies be made to develop ESR for

the recycling of "tin cans", especially those with a soldered seam and aluminum tops. The application of ESR to the purification of the metal fraction from municipal wastes should also be studied.

6. From our mechanical properties studies we confirmed that the copper and tin content of steel scrap should be kept to a minimum in order to prevent hot shortness during hot rolling. The adverse effects of low concentrations of chromium as well as of copper, nickel and tin on the drawability of steel was not confirmed in this work. From the results of these studies we recommend that a re-evaluation of the tolerance limits for some of these impurities on the drawing quality of mild steel is in order.

7. We recommend that further studies be made of the shredding and magnetic separation operations used in auto scrap processing so that better quality control of the melt stock can be made. We also recommend that research should be initiated towards developing a convenient method of physically separating pieces of cast iron and mild steel in shredded scrap. The separation of the scrap into two fractions would help control the gas loads during remelting and the carbon content of the refined ingot.

LIST OF INVENTIONS

1. A disclosure for a patent concerning a "Method of Converting Scrap Metal to Stainless Steel" has been filed with the USAEC Patent Division.

2. A paper entitled "Predicting Effects of Metallic Impurities on Formability of Low Carbon Steel" by C.V. Owen, F.A. Schmidt, and O.N. Carlson has been written and will be submitted for journal publication.

3. A paper entitled "Studies on the Metallurgical Upgrading of Automotive Scrap" by O.N. Carlson and F.A. Schmidt will be presented at the Environmental Control Session of the Annual AIME meeting, February, 1974, at Dallas, Texas.

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PERSONNEL DIRECTLY ASSOCIATED WITH PROJECT

Dr. O. Norman Carlson, Senior Metallurgist and Principal Investigator.

Frederick A. Schmidt, Metallurgist and Project Coordinator.

Charles V. Owen, Assistant Metallurgist and Supervisor. Mr. Owen was responsible for the preparation of simulated and actual compacts of auto scrap and various alloy preparations. He was also in charge of the vacuum arc melting operation, the mechanical testing program, and the induction melting in 1972-73 (3/4 time).

Dr. James McClusky, Postdoctoral Associate. Dr. McClusky was funded by the Rockefeller Foundation Grant during the 1971-72 period. His responsibilities included the vacuum induction melting and electroslag remelting of simulated auto scrap. He left the project in July 1972 (Full time).

Dr. Robert Shaw, Postdoctoral Associate. Dr. Shaw replaced Dr. James McClusky for the 1972-73 period of this project. He worked primarily on the electroslag remelting of auto scrap. (Full time).

Earl Ritland, Principal Technician. Mr. Ritland performed the actual operations and maintained the equipment associated with electron beam melting, consumable and nonconsumable electrode arc melting and electroslag remelting. He was also involved in sampling of the various ingots. (1/2 time).

Robert Lichtenberg, Graduate Assistant. Mr. Lichtenberg was also funded under the Rockefeller Foundation Grant for the 1971-72 period. During 1972-73 he was funded by the EPA grant and worked on the electroslag remelting as a means of purifying auto scrap. (1/2 time).

Erma Miller, Secretary. Mrs. Miller was responsible for typing reports, proposals, correspondence, etc. (1/5 time).

Michael Hartman, Undergraduate senior in Metallurgy. Mr. Hartman helped with the preparation of the simulated compacts of auto scrap. (~20 h/wk). He graduated and left the project in March 1972.

Everett Lewis III, Freshman, Research Helper. His duties included assisting in various melt operations and ingot sampling. (~10 h/wk). He also left the project in March 1972.

David Adams, Undergraduate senior in Metallurgy. Mr. Adams replaced Mr. Hartman and prepared the various compacts of actual auto scrap and helped with the mechanical testing. (~15 h/wk).

John Peterson, Research Technician. Mr. Peterson assisted in the various melting operations and did machinist work for special needs. He also helped with the sampling of ingots for chemical analysis. He left the project in September 1972. (1/? time).

Lanny Lincoln, Research Technician. Mr. Lincoln replaced Mr. Peterson during the 1972-73 period. He assisted in the various melting operations, welding of electrodes and assisted in the sampling of ingots. (1/2 time).

Analytical Chemist, the part time services of several chemists in our Spectroscopic and Analytical Service Groups made up this position.